the anomalous NMR spectrum of $Mg(acac)_2$ may be due to the presence of monomeric and oligomeric complexes rather than that of geometrical isomers. For example by making allowance for solvent-induced shifts[13] the 2.01 resonance in $CDCl_3$ solution may be classified with the observed shifts in the polar solvents[3] and attributed to monomer whereas the broad resonance at 1.80 can be attributed to oligomer. This is supported by the temperature dependence of the spectral profile which shows that the 2.01:1.80 ratio of resonance areas increases with temperature corresponding to dissociation of the oligomer. The apparent absence of complete reversibility suggests that the rate of attainment of monomer–oligomer equilibrium is slow. The broadness of the 1.80 resonance is consistent with a slow ligand-exchange broadening in the dimer. This interpretation also implies that $Ca(acac)_2$ and $Ba(acac)_2$ are oligomeric (methyl resonances at 1.78 and 1.77, respectively) in chloroform solution. There are no apparent steric restrictions to the formation of $Mg(acac)_2$ oligomers, since the ionic radius of the Mg^{2+} ion is slightly greater than those of Co^{2+} and Ni^{2+} [14] both of which exist as oligomers in the solid state and in solution in nonpolar solvents.[15] The small ionic radius of Be^{2+} [14] almost certainly precludes oligomerization which requires an increase in coordination number over that of the monomeric species.

Registry No. $Lu(acac)_3$, 17966-84-6; $Pr(acac)_3$, 14553-09-4; $Nd(acac)_3$, 14589-38-9; $Sm(acac)_3$, 14589-42-5; $Eu(acac)_3$, 14284-86-7; $Gd(acac)_3$, 14284-87-8; $Tb(acac)_3$, 14284-95-8; $Dy(acac)_3$, 14637-88-8; $Ho(acac)_3$, 14589-33-4; $Er(acac)_3$, 14553-08-3; $Yb(acac)_3$, 14284-98-1.

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Oxygenation Studies of Manganese(II) Complexes Containing Linear Pentadentate Ligands

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Manganese(II) complexes incorporating linear pentadentate O_2N_3 ligands have been synthesized and characterized. The reactivity of these materials in a variety of solvents with molecular oxygen suggests that several types of oxidation processes may be occurring. The rate of O_2 uptake is a function of the substituent on the central nitrogen donor as well as the substituent on the salicylaldehyde aromatic ring. Evidence is presented to show that irreversible oxidation of Mn(II) to Mn(III) occurs along with oxidation of the ligand. Two compounds of formulas $Mn(5\text{-}NO_2SALDPT)(OH)$ and $Mn(5\text{-}NO_2SALMeDPT)(OH)$ are isolated from their oxygenation reactions and characterized.

Introduction

The interaction of manganese with dioxygen has been theorized to be important in a number of processes of biological[1,2] and industrial[3] importance although the nature of these interactions is not well understood. The employment of model manganese compounds in order to study their interaction with oxygen is relatively unexplored although interest in this area is expanding. Manganese(II) phthalocyanine (Pc) in the presence of various nitrogeneous bases[4] is known to react with dioxygen to yield (B)(Pc)Mn–O–Mn(Pc)(B) which has been established via x-ray analysis.[5] Oxygenation of a pyridine solution of [*N*,*N'*-(1,3-propane)disalicylaldimine]manganese(II) is reported to yield also via x-ray analysis[6] a di-μ-hydroxy species containing the nonplanar quadridentate ligand. However, the x-ray and magnetic data do not allow an unambiguous choice between a di-μ-hydroxo or di-μ-oxy species. Three types of complexes involving $Mn^{III}–O_2–Mn^{III}$, $(Mn^{IV}–O–)_n$, and $Mn^{IV}{=}O$ have been postulated[7] to be obtainable upon reacting [*N*,*N'*-(1,2-ethane)disalicylaldimine]manganese(II) with molecular oxygen in various organic solvents. More recently it has been demonstrated[8] that *meso*-tetraphenylporphyrin(pyridine)manganese(II) and dioxygen interact at −79 °C in toluene solutions to yield an ESR-detectable reversible dioxygen adduct which irreversibly oxidizes at room temperature to an unidentified product. In this regard we wish to report a detailed study of the oxygenation of manganese(II) complexes employing a series of analogous Schiff base pentadentate ligands.

Experimental Section

Materials. 3,3′-Bis(aminopropyl)-*N*-methylamine (CH_3DPT), 3,3′-bis(aminopropyl)-*N*-propylamine (PrDPT), and 3,3′-bis(aminopropyl)-*N*-phenylamine (PhDPT) were pepared by a modified method described by Braunholtz and Mann.[9] 3,3′-Bis(aminopropyl)amine (DPT) was obtained from Aldrich Chemical Co., salicylaldehyde (SAL) was obtained from Fisher Scientific Co., and 5-nitrosalicylaldehyde ($5\text{-}NO_2SAL$) and 5-chlorosalicylaldehyde (5-ClSAL) were obtained from Eastman Chemical Co., and each was used without further purification. 5-Bromosalicylaldehyde (5-BrSAL) was prepared by a method previously described.[10] 3-Methoxysalicylaldehyde (3-MeOSAL) from Eastman Chemical Co. was vacuum-distilled prior to use.

Preparation of the Mn(XSALDPT) and Mn(XSALMeDPT) Complexes. Due to the instability of solutions of these Mn(II) complexes in air the complexes were prepared under nitrogen in order to ensure each sample's integrity. The general method of preparation was as follows. To a stirring solution of the appropriate aldehyde (0.02 mol) in 30 mL of *tert*-butyl alcohol was added the appropriate amine (0.01 mol) dissolved in 30 mL of *tert*-butyl alcohol. After stirring of the mixture for $^1/_4$ h potassium hydroxide (0.02 mol) dissolved in 10 mL of distilled water was added. The resulting solution was refluxed for $^1/_2$ h after which the solution still under nitrogen was cooled to room temperature. To this solution was added dropwise $Mn(C_2H_3O_2)_2{\cdot}4H_2O$ (0.01 mol) dissolved in 20 mL of distilled, oxygen-free H_2O. In all cases a bright yellow or orange precipitate

Table I. Elemental Analysis Data

	% C		% H		% N		μ_{eff}, μ_B
	Found	Calcd	Found	Calcd	Found	Calcd	
[Mn(5-ClSALDPT)]($CHCl_3$)	43.4	43.5	4.4	3.9	7.3	7.3	5.92
[Mn(5-BrSALDPT)](H_2O)	42.3	42.9	3.8	4.0	7.4	7.4	5.94
Mn(5-NO_2SALDPT)	49.4	49.8	4.7	4.4	14.1	14.5	5.91
[Mn(5-NO_2SALDPT)](THF)$_{0.5}$	51.0	51.0	4.9	4.8	13.5	13.5	5.86
[Mn(5-NO_2SALDPT)]($CHCl_3$)$_{0.5}$	45.4	45.4	4.0	4.0	12.7	12.9	5.89
[Mn(3-CH_3OSALDPT)](H_2O)$_2$	54.7	54.1	5.8	6.4	8.4	8.6	5.85
Mn(5-BrSALMeDPT)	44.6	44.7	4.2	4.1	7.0	7.4	6.02
Mn(5-NO_2SALMeDPT)	50.8	50.8	5.3	4.6	13.7	14.1	5.73
Mn(SALPrDPT)	63.8	63.5	7.6	7.0	10.3	9.7	5.89
Mn(SALPhDPT)	66.5	66.5	6.0	6.0	8.8	8.9	5.85
Mn(5-NO_2SALDPT)(OH)	48.0	48.2	4.1	4.2	13.9	14.1	4.91
Mn(5-NO_2SALMeDPT)(OH)	48.6	49.1	4.4	4.4	13.5	13.4	4.86
[Mn(3-CH_3OSALDPT)(OH)](H_2O)	53.9	54.3	5.5	6.0	8.7	8.6	5.29

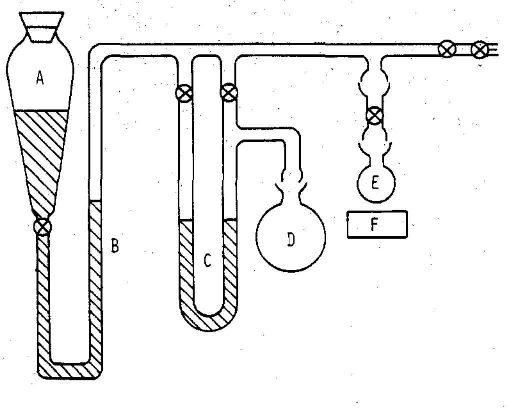
formed. The solution was stirred for $1^1/_2$ h after the Mn addition was completed. Following this the reaction flask was taken into an inert-atmosphere box and the contents isolated via filtration. In all cases the product was washed with hexane and dried in vacuo over anhydrous $CaCl_2$ for a minium of 12 h. Analytical results for these compounds are presented in Table I.

Preparation of Mn(SALPrDPT) and Mn(SALPhDPT). To a solution of 0.02 mol of salicylaldehyde dissolved in 25 mL of a mixture of 50:50 (v/v) isopropyl and *tert*-butyl alcohols was added 0.01 mol of the appropriate amine dissolved in 25 mL of the 50:50 alcohol solution. The mixture was stirred for $^1/_2$ h followed by addition of 0.02 mol of KOH dissolved in 10 mL of distilled H_2O. The mixture was brought to reflux under nitrogen for $^1/_2$ h and then cooled to room temperature. To this solution was added dropwise 0.01 mol of $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ dissolved in 20 mL of distilled, deoxygenated water. A yellow precipitate formed immediately upon the addition of the manganese solution. The mixture was stirred $^1/_2$ h after manganese addition was completed. Following this the reaction flask was taken into an inert-atmosphere box and the contents isolated via filtration. The product was washed with isopropyl alcohol and hexane and dried in vacuo over anhydrous $CaCl_2$ for a minimum of 12 h.

Preparation of Solvent Adducts of Mn(5-NO_2SALDPT). A saturated solution of Mn(5-NO_2SALDPT) was prepared in either THF or $CHCl_3$ in an N_2 atmosphere. After filtration the orange solutions were allowed to stand for several days after which orange crystals had formed. These were isolated and dried in vacuo over anhydrous $CaCl_2$ at room temperature.

Preparation of Oxygenated Products. To 50 mL of toluene was added approximately 1.0 g of Mn(5-NO_2 SALRDPT) in an inert-atmosphere facility. The resulting suspension was then exposed to O_2 for 6 h under 810 Torr. The resulting material, Mn(5-NO_2SALRDPT)(OH), was isolated by filtration and dried at 100 °C in vacuo.

Physical Measurements. Oxygen-uptake measurements were obtained with a modified Warburg apparatus[11] shown in Figure 1. The compounds were exposed to approximately 800 Torr O_2 pressure while in the solid state and were suspended or dissolved in degassed toluene, diglyme, or pyridine. The volume of oxygen absorbed was monitored by equilibrating the pressure inside the reaction chamber with the constant pressure in the reference arm. The amount of O_2 absorbed was then calculated employing the ideal gas equation after correcting for the vapor pressure of the solvent and the volume of oxygen absorbed by the degassed solvent. Infrared spectra were obtained in the 4000–500-cm^{-1} range using a Beckman Model 20A-X spectrophotometer. Solid-state spectra were recorded as Nujol mulls. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-7 double-focusing mass spectrometer using a solid inlet probe. The solid probe temperature was maintained at a value to prevent decomposition of the samples. The source temperature was maintained at approximately the temperature of the solid probe. Analyzer tube and ion source pressures of less than 10^{-6} Torr were employed. Where necessary, spectra were calibrated with perfluorokerosene. Duplicate elemental analyses were performed in this laboratory using a Perkin-Elmer Model 240 carbon–hydrogen–nitrogen analyzer. ESR spectra were taken on a Varian Model E-12 X-band spectrometer equipped with a Varian E-101 microwave bridge. Cooling of the sample was performed by using cold nitrogen gas and temperature was controlled by adjusting the nitrogen flow and monitoring a copper–constantan thermocouple. The field and frequency calibrations were made using DPPH powder (g = 2.0036). Thermal gravimetric analyses (tga) were performed using a Cahn RG Electrobalance with a Stone S-101 programmer, S-601 amplifier, and LD-202 recorder–controller.



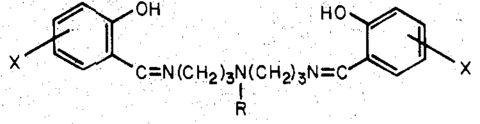
OXYGEN UPTAKE APPARATUS

A: Mercury reservoir; B: 50 mL buret for measuring O_2 consumption; C: Manometer for measuring changes in pressure; D: Reference flask; E: Reaction Flask (50 mL); F: Magnetic stirrer.

Figure 1. Oxygen-uptake apparatus.

Results and Discussion

A series of manganese(II) complexes which incorporate linear potentially pentadentate ligands have been prepared by the interaction of aqueous solutions of $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ with alcohol solutions of preformed deprotonated pentadentate ligands under a nitrogen atmosphere. The ligands employed are condensation products of variously substituted salicylaldehydes (5-Cl, 5-Br, 3-CH_3O, 5-NO_2) and triamines which differ only in the group attached to the middle nitrogen, structure I. Yellow complexes of general formula Mn(XSALRDPT) are isolated in each case. An examination of the elemental analysis data in Table I indicates that several of the compounds are hydrates, or in the case of 5-ClSALDPT a $CHCl_3$ solvate is produced after recrystallization of the material from chloroform. Subsequent to this work Sacconi and Bertini[12] reported the synthesis of two similarly formulated materials: Mn(SALDPT) and Mn(5-ClSALMeDPT). Mn(SALMeDPT) was also isolated in their study but the



Ia, R = H; XSALDPT
b, R = CH_3; XSALMeDPT
c, R = n-C_3H_7; XSALPrDPT
d, R = C_6H_5; XSALPhDPT

compound was reported to decompose too rapidly to allow physical measurements. The reactivity of these three complexes with O_2 was not investigated.

All reported manganese(II) complexes readily dissolve in $CHCl_3$, tetrahydrofuran, pyridine, and other related organic solvents to yield yellow solutions which immediately darken on exposure to O_2. Sensitivity to O_2 in the solid state is minimal over a 24-h period except for the 3-CH_3O derivatives.

Additional support for the suggested formulations is provided by infrared and mass spectral analyses. Infrared data were obtained as Nujol mulls on all complexes. For those known to be air sensitive, the mulls were prepared in an inert atmosphere and the spectra were obtained without delay. The Mn(SALDPT) complexes show the characteristic sharp N–H stretch at 3250 cm^{-1} suggestive of a bonded secondary nitrogen. Both Mn(XSALDPT) and Mn(XSALRDPT) show a sharp band at 1625 cm^{-1} characteristic of a coordinated imine. In the compounds formulated as hydrates the characteristic band around 3400 cm^{-1} for water is observed. The 3-CH_3O-substituted complexes show a sharp band around 800 cm^{-1} indicative of a 1,2,3-trisubstituted benzene nucleus.[13] The 5-NO_2 substituted complexes show the characteristic NO_2 bands at 840–700 cm^{-1}.[8]

Mass spectral results indicate that a distinct relatively intense parent ion cluster is observable for every complex. Little or no decomposition of the solid sample occurs at the temperature required to observe a spectrum. Water of hydration suggested by infrared data and analytical results is not observed in the mass spectra. Fragmentation patterns of each complex are strikingly similar regardless of the ligand substituent. The absence of an appreciable signal at an m/e corresponding to the free ligand suggests that the manganese ion is tightly bound to the dinegative ligand. These observations are in agreement with previous results[16] obtained on analogous cobalt(II), nickel(II), and copper(II) complexes.

A magnetic moment ca. 5.92 μ_B is expected for a high-spin Mn(II) complex. It can be seen from Table I that the Mn(II) complexes all exhibit a magnetic moment in this range indicative of high-spin Mn(II). This is in agreement with previously published results[12] on Mn(SALDPT). The complexes also give rise to ESR spectra both in the solid state and in frozen and fluid solution typical of high-spin manganese(II).

Oxygen Reactivity. The reported manganese(II) complexes quickly react with molecular oxygen when the compounds are dissolved or suspended in a solvent. Yellow solutions of each complex quickly (~1 min) discolor upon exposure to O_2. At first glance no difference is expected between Mn(XSALDPT) vs. Mn(XSALMeDPT) in their reactivity toward O_2. Such, however, is not the case. In all instances except the 5-nitro-substituted derivatives, which will be discussed later, the Mn(XSALDPT) complexes follow a different reactivity pattern in their interaction with O_2 than do the Mn(XSALMeDPT) complexes.

The extent and rate of O_2 uptake for Mn(XSALDPT) complexes incompletely dissolved in toluene are observed to be a function of the substituent on the salicylaldehyde ring (Figure 2). While the 5-nitro derivative quickly (within $^1/_2$ h) consumes approximately 0.5 mol of O_2/mol of Mn and ceases, the other derivatives continue to take up O_2 indefinitely. Electron-donating groups promote more extensive O_2 uptake than electron-withdrawing groups for a specific time period. In an effort to learn more about the nature of the oxygenation reaction numerous attempts were made to isolate a product from these reactions. Unfortunately our attempts were not fruitful for X = H, 5-Cl, 5-Br, and 3-CH_3O. In these cases an undefinable dark brown unfilterable material was obtained. Electron spin resonance (ESR) measurements of frozen and fluid reaction solutions at various stages of oxygenation gave no discernible signals in contrast to the manganese(II) precursor which was ESR active. Our failure to observe an ESR signal could be construed as evidence for the presence of Mn(III) and the absence of Mn(IV).

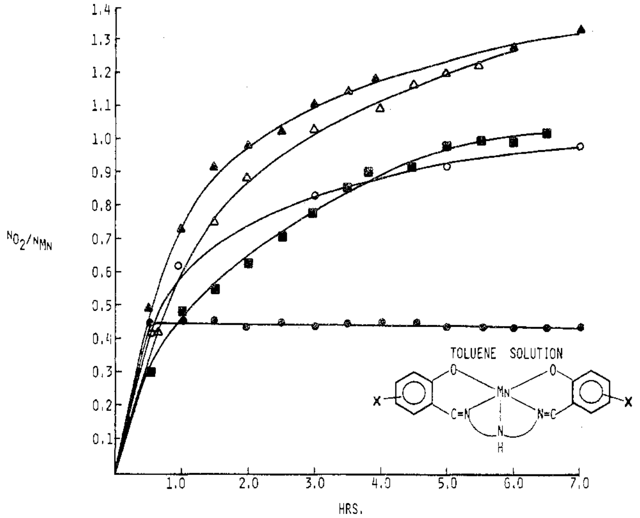


Figure 2. Oxygenation of Mn(XSALDPT) in toluene solution. P_{O_2} = 790 Torr. ●, X = 5-NO_2; ■, X = 5-Cl; ○, X = 5-Br; △, X = H; ▲, X = 3-MeO.

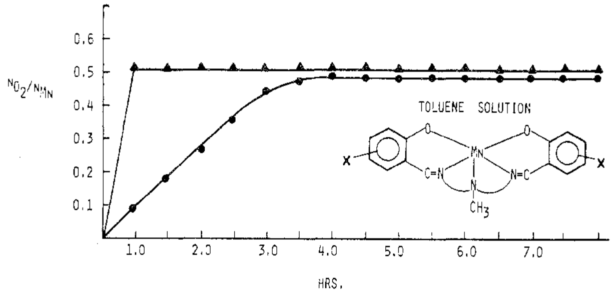


Figure 3. Oxygenation of Mn(5-NO_2SALMeDPT) (▲) and Mn(SALMeDPT) (●) in toluene solution. P_{O_2} = 790 Torr.

Oxygenation of toluene solutions of Mn(XSALMeDPT) complexes for relatively short periods is more straightforward. Uptake of O_2 appears to be complete after 6 h corresponding to an O_2:Mn ratio of approximately 0.5 regardless of the salicylaldehyde substituent. Figure 3 graphically illustrates two of these measurements. ESR results were identical with those described for oxygenated Mn(XSALDPT). Attempts to isolate any oxidized material were again unsuccessful for X = H, 5-Cl, and 5-Br. Oxygenation studies on Mn(SALPrDPT) and Mn(SALPhDPT) in toluene gave similar results although over a much longer time period.

A comparison of the reaction rates of the Mn(XSALDPT) and Mn(XSALMeDPT) complexes toward O_2 reveals reactivity differences. There appears to be little or no substituent effect in the initial uptake of O_2 in either complex (i.e., conversion of Mn(II) to Mn(III)). On the other hand, there is a pronounced substituent effect in the rate of further O_2 reaction in the case of Mn(XSALDPT). The rate for X = 5-NO_2 appears to be zero whereas for other reactive substituents the trend is 5-Br < 5-Cl < H < 3-CH_3O. The nature of this further reactivity with O_2 is not known. We suggest that it may be due to irreversible oxidation of the coordinated ligand at the secondary amine site catalyzed by manganese ion. Support for this conclusion comes from the fact that Mn(XSALRDPT) complexes do not exhibit this additional O_2 reactivity over the same time period. Numerous factors could be affecting this difference but one explanation could be linked to the chemistry of a coordinated N–H vs. that of

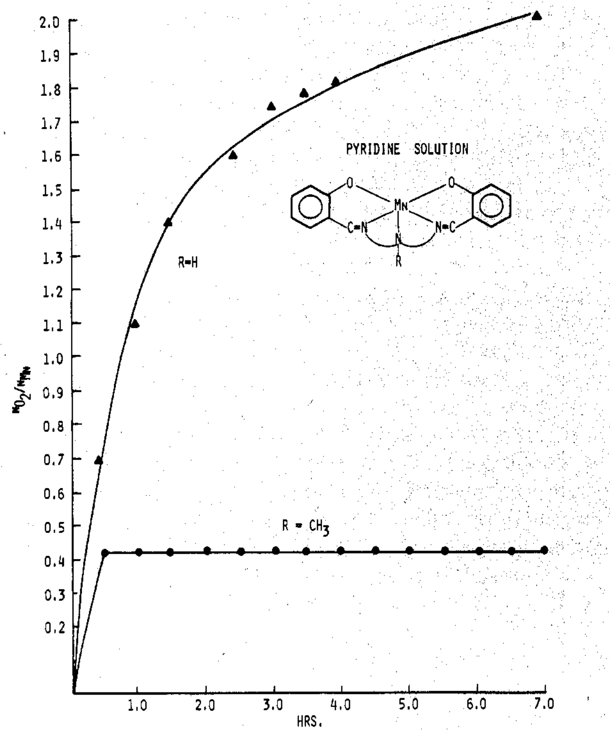


Figure 4. Oxygenation of Mn(SALDPT) and Mn(SALMeDPT) in pyridine solution. P_{O_2} = 790 Torr.

a coordinated N–R group. Mn(II) is known to promote the oxidation of organic materials including amines.[15] Upon coordination of the amine the nitrogen–hydrogen bond strength is reduced as evidenced by the shift in the N–H stretch in the infrared spectrum. Reduction of the N–H stretching frequency would render the N–H group more reactive and hence possibly more susceptible to oxidation. This phenomenon is not possible in the RDPT derivatives. A second explanation regarding this reactivity difference could be due to the slight differences in toluene solubility of Mn(XSALDPT) and Mn(XSALRDPT) complexes. Oxygenation in pyridine, however, where both types of complexes are very soluble produces indentical results (Figure 4). Finally, a similar oxygenation reactivity has been observed in analogous cobalt(II) complexes[16] and attributed to irreversible oxidation of the coordinated secondary amine of DPT.

As an alternate rationalization the solvent may be undergoing oxidation in the presence of the oxidized manganese complex. For example it has been reported[17] that $Mn(C_2H_3O_2)_3$ will catalyze the oxidation of toluene by O_2 to yield a variety of products such as benzaldehyde, benzoic acid, etc. In an effort to shed more light on the nature of this additional oxygen uptake, long reaction periods in toluene were monitored employing Mn(SALRDPT). As peviously stated an initial O_2 uptake corresponding to 0.5 mol of O_2/mol of Mn occurs within 6 h. No additional O_2 is consumed during the next approximately 25 h; however, surprisingly O_2 uptake resumes after this "delay" and continues indefinitely. Duplicate experiments on Mn(SALMeDPT) and Mn(SALPrDPT) in toluene gave identical results. In hopes of attributing these observations to a manganese-catalyzed oxidation of the solvent we performed the oxygenation experiments in diglyme where the complexes possess more solubility. Again a rapid uptake of O_2 to $n_{O_2}/n_{Mn} = 0.5$ followed by an induction period and then resumption of O_2 absorption was observed. The only difference between toluene and diglyme is that the induction period for diglyme is less than that for toluene. Extended oxygenation periods (2–3 days) in pyridine with the same complex also gave identical results. A similar effect must be occurring in all solvents since the rate of O_2 uptake after the induction period is the same. The tendency for all solvents to undergo oxidation is no doubt quite different; therefore, the aliphatic carbon chain in the SALRDPT ligand is suspected of being dehydrogenated. Precedence for such reactivity can be found in the oxidation of lupin alkaloids.[18] It should be noted that although the rate of initial oxygenation is relatively constant, secondary oxygenation is considerably slower for Mn(SALPhDPT) than for Mn(SALMeDPT) or Mn(SALPrDPT).

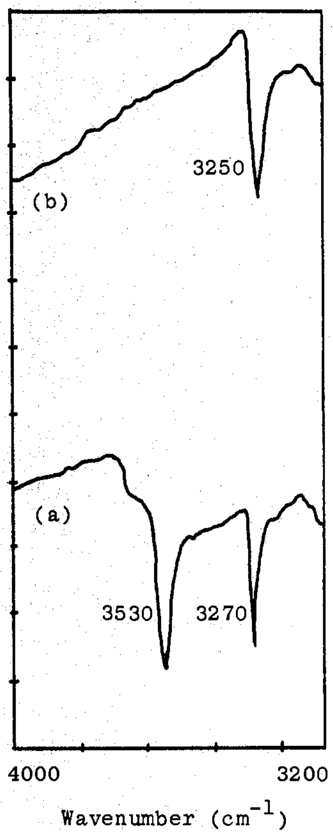


Figure 5. Nujol-mull infrared spectra of Mn(5-NO_2SALDPT)(OH) (a) and Mn(5-NO_2SALDPT) (b).

As referred to several times earlier the reactions of Mn(5-NO_2SALDPT) and Mn(5-NO_2SALMeDPT) with O_2 are a case unique unto themselves when compared to the other derivatives. Reactions with O_2 were carried out under the same conditions as for the other derivatives but in the nitro cases a product was isolable as well as characterizable. Both compounds take up an initial amount of O_2 equal to a ratio of 0.5 (O_2:Mn) with no further O_2 uptake, suggesting a manganese:oxygen ratio of 1:1. A comparison of the ESR spectra of precursor solutions exposed to O_2 with those prepared in an inert atmosphere again suggests that Mn(II) has been oxidized to Mn(III).

Magnetic susceptibility measurements on the oxidized products reveal in both cases a drop of $\sim 1.0\ \mu_B$ from the value of the starting material. The experimental magnetic moments are close to the calculated value for high-spin d^4 systems indicating the presence of Mn(III). Elemental analysis results suggest a formulation of [MnL]O or [MnL]OH. Close scrutiny of the infrared spectra of each precursor and its oxygenated product reveals that the Mn(III) complex has a peak at 3530 cm^{-1} which is absent in the Mn(II) complex (Figure 5). Absorption bands in this area are associated with an OH stretching frequency. Further comparison of the IR spectra also shows the presence of a new band in the Mn(III) complex around 620 cm^{-1} (Figure 6). This band can be assigned to a Mn–O stretch.[7,19] Further evidence for the Mn–OH species

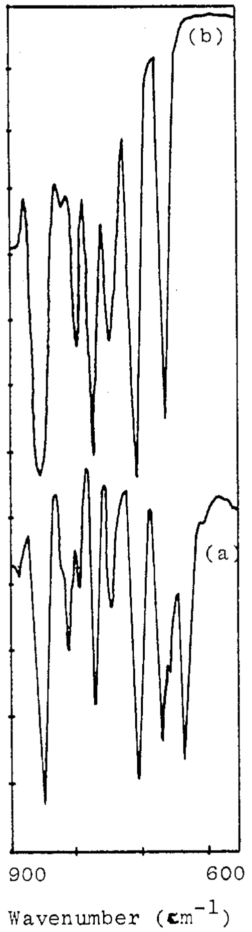
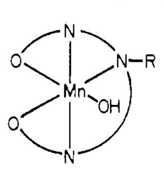


Figure 6. Nujol-mull infrared spectra of Mn(5-NO_2SALDPT)(OH) (a) and Mn(5-NO_2SALDPT) (b).

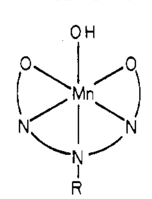
exists in the appearance of a band at 1022 cm^{-1} attributable to a metal–hydroxy bend[20] which again is absent in the starting material. At first it was though that the 3530-cm^{-1} band could be due to coordinated water. An infrared spectrum of the material dried at 100 °C in vacuo was superimposable on that of the undried specimen; hence the band is believed to not be due to water. To test the validity of the OH bound to Mn the following experiment was conducted. A stream of dry O_2 was passed through a reservoir of D_2O by vigorous bubbling. This D_2O-saturated O_2 was then bubbled through a dry toluene suspension of Mn(5-NO_2SALDPT) for 6 h under 800 Torr. The compound was isolated and dried at 100 °C in vacuo. Its infrared spectrum showed a shift in the peaks shown in Figure 4 to 2615 and 2420 cm^{-1} from 3530 and 3270 cm^{-1}, respectively. Calculated values based on the relation $\nu_{OH}/\nu_{OD} = 1.35$ give 2614 and 2422 cm^{-1}, respectively. Consequently this evidence shows the shift expected when the hydroxyl hydrogen exchanges with a deuterium and suggests that the complex may be formulated as Mn–OH. In addition it was possible to cause the exchange by dissolving Mn(5-NO_2SALDPT)(OH) in THF and treating with NaOD. Results of thermal gravimetric analyses (tga) on the oxidation products of the nitro derivatives reveal significant weight loss at 170 °C. (Calcd for loss of weight equivalent to 17 atomic mass units prior to sample decomposition: Mn(5-NO_2SALDPT)(OH), 3.42%; Mn(5-NO_2SALMeDPT)(OH), 3.31%. Found: 3.23% and 3.56%, respectively.)

The reported manganese(II) complexes in this study are unreactive toward dioxygen in the solid state in contrast to a related investigation[18] directed at tetradentate Schiff base chelates of manganese(II). Greater than 72 h is required before any measurable O_2 uptake is observed. The sole exception to this phenomenon is Mn(3-CH_3OSALDPT)$(H_2O)_2$ which consumes approximately 0.53 mol of O_2/mol of Mn over an 18-h period. Infrared data on the green material yield a sharp absorption at 3610 cm^{-1} suggesting an O–H stretch. A magnetic moment on this ESR-inactive material of 5.29 μ_B while slightly higher than usual is consistent with a Mn(III) ion. A two-step weight loss occurring at 130 and 190 °C via tga analysis along with elemental analysis data support the following analogous formulation: Mn(3-CH_3OSALDPT)(OH)·H_2O. The presence of H_2O is confirmed by IR analysis. Neither the comparable complex Mn(3-CH_3OSALMeDPT) nor its oxidized product could be prepared analytically pure. What we believed to be Mn(3-CH_3OSALMeDPT) rapidly changed from yellow to green during all isolation attempts in our inert atmosphere facility (~1 ppm of O_2).

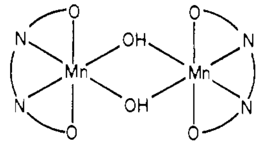
Structural evidence for the isolable oxidized products is not available; however, a mononuclear six-coordinate structure is envisioned wherein the hydroxyl group and the N_3O_2 pentadentate ligand occupy the inner coordination sphere of manganese(III). The conformation of the pentadentate ligand is unknown; however, it is reasonable to assume that it may be the same as found in $[Co(SALDPT]_2O_2{\cdot}C_6H_5CH_3$[21], IIA,



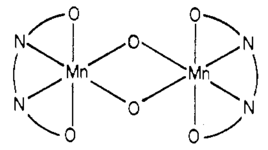
IIA



IIB

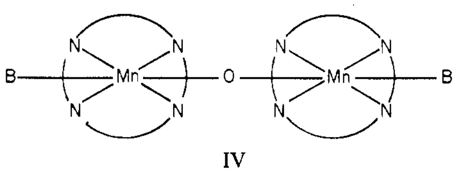


IIIA



IIIB

since the cobalt(II) and manganese(II) precursors are known[12] to be isomorphous. On the other hand, the conformation shown in IIB must be considered in light of the fact that [Co(SALDPT)Imid)]Br[22] (Imid = imidazole) adopts this arrangement. A dinuclear structure similar to that of the oxygenation product, IIIA, of Mn(SALTM) in pyridine[6] or that of the reaction product,[23] IIIB, of manganese(III)–Schiff base complexes with aqueous base seems unreasonable in this case because of the lack of two vacant sites in Mn(5-NO_2SALRDPT). An oxo-bridged structure analogous to the oxygenation product[5] of manganese(II) phthalocyanine, IV,



IV

can also be ruled out because of the high-spin nature of the Mn(III) and $n_{O_2}/n_{Mn} = 0.5$ in Mn(5-NO_2SALRDPT).

It is interesting to speculate concerning the mechanism whereby these oxygenations occur. Specifically one wonders if there is a superoxo (Mn^{3+}–O_2^-), mononuclear peroxo (Mn^{4+}–O_2^{2-}), or dinuclear peroxo (Mn^{3+}–$(O_2)^{2-}$–Mn^{3+}) intermediate produced which quickly reacts with moisture to produce Mn^{3+}–OH^-. All efforts to observe a transient paramagnetic species via ESR during all stages of the oxygenation were unsuccessful. This observation could conceivably suggest the absence of a superoxo intermediate; however, spin–spin coupling between the high-spin manganese(III) and superoxide anion may serve to eliminate such an ESR signal. Employing rigorously dry O_2 and toluene yields a product which contains no O–H stretch or Mn–OH deformation in its infrared spectrum. The addition of H_2O to this material dissolved in an appropriate organic solvent gives a compound similar to Mn(5-NO_2SALDPT)(OH). Preliminary analytical and spectroscopic evidence suggests that a peroxo species is the initial product.[24] Consequently we propose the tentative mechanistic scheme given by eq 1–4 recognizing that eq 4 is

$$Mn^{2+}L + O_2 \rightarrow LMn^{3+}O_2^- \quad (1)$$

$$LMn^{3+}O_2^- + Mn^{2+}L \rightarrow LMn^{3+}(\text{-O-O-})^{2-}Mn^{3+}L \quad (2)$$

$$LMn^{3+}(\text{-O-O-})^{2-}Mn^{3+}L + 2H_2O \rightarrow 2LMn^{3+}\text{-OH} + H_2O_2 \quad (3)$$

$$LMn^{3+}\text{-OH} + [O] \rightarrow L'Mn^{3+}\text{-OH} \quad (4)$$

significant in the early stages only for Mn(XSALDPT) and that L′ corresponds to an oxidized product of XSALDPT.

In summary, evidence has been presented which shows the irreversibility of the reaction between O_2 and Mn(II) complexes containing a pentadentate O_2N_3 ligand field. In the majority of cases reaction with O_2 does not stop with conversion to Mn(III) but continues with oxidation of the ligand even under strictly anhydrous conditions. Oxidized products from nonanhydrous reactions are isolated for the nitro-substituted complexes which have the formulation Mn(5-NO_2SALDPT)(OH) and Mn(5-NO_2SALMeDPT)(OH).

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Registry No. Mn(5-ClSALDPT), 61916-28-7; Mn(5-BrSALDPT), 61916-11-8; Mn(5-NO_2SALDPT), 61916-12-9; Mn(3-CH_3OSALDPT), 61916-13-0; Mn(5-BrSALMeDPT), 61951-29-9; Mn(5-NO_2SALMeDPT), 61916-14-1; Mn(SALPrDPT), 61916-15-2; Mn(SALPhDPT), 61916-16-3; Mn(5-NO_2SALDPT)(OH), 61967-10-0; Mn(5-NO_2SALMeDPT)(OH), 61916-17-4; Mn(3-CH_3OSALDPT)(OH), 61916-18-5; Mn(SALDPT), 15378-52-6; Mn(SALMeDPT), 61916-19-6.

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Infrared and Crystal Structure Study of σ vs. π Bonding in Tetrahedral Zinc(II) Complexes. Crystal and Molecular Structures of Dichlorobis(4-substituted pyridine)zinc(II) Complexes

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The crystal structures of three $ZnCl_2$(4-R-py)$_2$ (py = pyridine) complexes where R = vinyl (vin), acetyl (ac), and cyano (CN) have been determined by x-ray techniques. The far-infrared spectra for the R = methyl, vinyl, acetyl, and cyano and the unsubstituted pyridine derivatives have also been measured. The Zn–N bond length in the $ZnCl_2$(4-R-py)$_2$ complexes is directly proportional to the ligand pK_b, suggesting that π-bonding effects are minimal in the series. The Zn–Cl bond distance is virtually independent of the ligand pK_b, where R is anything but an H atom. $ZnCl_2$(4-H-py)$_2$ has longer Zn–Cl distances presumably because of a unique packing arrangement. The trends found in the structural studies are not obvious from the infrared data regarding chemical bonding. The complex $ZnCl_2$(4-vin-py)$_2$ crystallizes in the triclinic space group $P\bar{1}$. The cell dimensions are $a = 7.501$ (4), $b = 7.522$ (5), and $c = 14.482$ (6) Å with $\alpha = 90.41$ (4), $\beta = 90.53$ (4), and $\gamma = 105.29$ (5)°. There are two molecules of the complex per unit cell. The final R value was 0.048 for the 1566 reflections used in the analysis. There are eight molecules of $ZnCl_2$(4-ac-py)$_2$ in a monoclinic cell, space group $C2/c$, with the dimensions $a = 19.340$ (15), $b = 18.084$ (18), and $c = 9.678$ (6) Å and $\beta = 100.13$ (5)°. The final R value was 0.052 for the 1067 reflections used in the analysis. The $ZnCl_2$(4-CN-py)$_2$ complex forms monoclinic crystals with the space group $I2/a$. There are eight molecules in the unit cell of dimensions $a = 17.229$ (2), $b = 7.443$ (9), and $c = 22.500$ (3) Å with $\beta = 90.53$ (1)°. The final R value was 0.048 for the 1602 reflections used in the analysis. The data for all three complexes were measured using a computer-controlled diffractometer. The radiation was from graphite-monochromatized molybdenum, and a variable-speed θ–2θ scan technique was used in the intensity measurements.

Introduction

The relative roles of σ vs. π bonding in zinc(II) complexes have generated considerable controversy. A study of the far-infrared spectra of a series of $ZnCl_2$(4-R-py)$_2$ complexes was reported to indicate that both the Zn–Cl and Zn–N bonds increased in strength with any substitution.[2-4] When R was more electron donating than hydrogen, the Zn–N σ-bond was strengthened, increasing the electron density on the zinc atom.