oxidation state. A phase is presently under investigation which clearly contains discrete six-atom metal clusters[25] (bond distances 3.21–3.23 Å), thus representing the end member of the metal–metal bonded series extending from isolated octahedral metal clusters through chains to two-dimensional sheets of shared metal octahedra. In addition the phase $ScI_{2.15}$ in a CdI_2-type structure evidently exhibits a metallic conduction for only single sheets of metal atoms.[26] Seldom has one element provided such a versatile and exciting opportunity to view metal–metal bonding and the properties derived thereby over such a range of structural complexity and, presumably, electron delocalization.

The didactic concept of cluster condensation recently put forth by Simon[27,28] to account for structural similarities in metal-rich compounds works quite well to describe the chains of shared but distorted octahedra in Sc_7Cl_{10}. However, the presence of isolated Sc(III) ions is not predicted or accounted for by this type of modeling. This new variation reveals another important dimension in the structure of metal-rich phases, one that emphasizes the need for electronic models to complement a geometric scheme of cluster condensation. Obviously the radial extension of 3d orbitals early in the series is favorable for metal–metal bonding, contrary to some expectations, but the richness and diversity of this feature with scandium requires further definition of more subtle factors than just the commonly accepted[29,30] orbital size.

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Registry No. Sc_7Cl_{10}, 61966-52-7.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Work performed for the U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.
(2) K. R. Poeppelmeier and J. D. Corbett, *Inorg. Chem*, **16**, 294 (1977).
(3) B. C. McCollum, M. J. Camp, and J. D. Corbett, *Inorg. Chem.*, **12**, 778 (1973).
(4) D. G. Adolphson and J. D. Corbett, *Inorg. Chem.*, **15**, 1820 (1976).
(5) J. G. Converse and R. E. McCarley, *Inorg. Chem.*, **9**, 1361 (1970).
(6) L. F. Bates, "Modern Magnetism", 3d ed, Cambridge University Press, Cambridge, England, 1951, pp 133–136.
(7) W. J. Rohrbaugh and R. A. Jacobson, *Inorg. Chem.*, **13**, 2535 (1974).
(8) R. A. Jacobson, "An Algorithm for Automatic Indexing and Bravais Lattice Selection. The Programs BLIND and ALICE", U.S. Atomic Energy Commission Report IS-3469, Iowa State University, Ames, Iowa, 1974.
(9) F. Takusagawa, personal communication, Ames Laboratory, 1975.
(10) D. G. Adolphson, J. D. Corbett, and D. J. Merryman, *J. Am. Chem. Soc.*, **98**, 7234 (1976).
(11) S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, **7**, 2124 (1968).
(12) P. Main, M. M. Woolfson, and F. Germain, "MULTAN, a Computer Program for the Automatic Solution of Crystal Structures", University of York Printing Unit, York, U.K., 1971.
(13) J. D. Scott, Queen's University, Kingston, Ontario, private communication, 1971.
(14) "International Tables for X-Ray Crystallography", Vol. III, 2nd ed, Kynoch Press, Birmingham, England, 1962.
(15) W. Klemm and E. Krose, *Z. Anorg. Allg. Chem.*, **253**, 218 (1947).
(16) $\chi_M{}^* = \chi_g M 7/6$ where M is the formula weight of $ScCl_{1.43}$, and the factor 7/6 accounts for the difference in types of metal atoms.
(17) D. A. Lokken and J. D. Corbett, *Inorg. Chem.*, **12**, 556 (1973).
(18) H. Schäfer and H. G. Schnering, *Angew. Chem.*, **76**, 833 (1964).
(19) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, pp 400, 410.
(20) R. J. Clark and J. D. Corbett, *Inorg. Chem.*, **2**, 460 (1963).
(21) J. D. Corbett, R. A. Sallach, and D. A. Lokken, *Adv. Chem. Ser.*, **No. 71**, 56 (1967).
(22) J. D. Greiner, J. F. Smith, J. D. Corbett, and F. J. Jellinek, *J. Inorg. Nucl. Chem.*., **28**, 971 (1966).
(23) F. H. Spedding and J. J. Croat, *J. Chem. Phys.*, **58**, 5514 (1973).
(24) The temperature dependence of the magnetic susceptibility of Sc was originally interpreted[23] in terms of a single localized 3d electron. However the polarized neutron diffraction behavior of scandium in an applied magnetic field is not consistent with this interpretation: W. C. Koehler and R. M. Moon, *Phys. Rev. Lett.*, **36**, 616 (1976).
(25) K. R. Poeppelmeier and J. D. Corbett, to be submitted for publication.
(26) B. C. McCollum and J. D. Corbett, *Chem. Commun.*, 1666 (1968).
(27) A. Simon, *Chem. Unserer Zeit*, **10**, 1 (1976).
(28) A. Simon, Hj. Mattausch, and H. Holzer, *Angew. Chem., Int. Ed. Engl.*, **15**, 624 (1976).
(29) J. C. Sheldon, *Aust. J. Chem.*, **17**, 1191 (1964).
(30) J. E. Ferguson, *Prep. Inorg. React.*, **7**, 93 (1971).

Contribution from the Department of Chemistry,
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Proton Magnetic Resonance Spectra of $Lu(acac)_3{\cdot}2H_2O$ in Solution

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^1H NMR spectra of $Lu(acac)_3{\cdot}2H_2O$ in several solvents are reported, where acac = $CH_3COCHCOCH_3^-$. The spectral profiles are temperature dependent in benzene and toluene solutions and the multiplicity of ligand methyl resonances is attributed to slow exchange between nonequivalent methyl groups in a dimeric structure. The temperature dependence in acetone solution is consistent with the presence of a monomer–dimer equilibrium with $\Delta H° = -28.2 \pm 1.5$ kJ mol^{-1} and $\Delta S° = -74.5 \pm 4.5$ J K^{-1} mol^{-1}. The single ligand methyl and 3-H resonances in the strongly coordinating solvents dimethyl sulfoxide and pyridine indicate the sole presence of solvated monomers. Previous proposals about the anomalous spectrum of $Mg(acac)_2$ in $CDCl_3$ are also discussed.

Recent investigations[1,2] of intermolecular energy transfer between the metal ions of lanthanide acetylacetonates in solution have shown that the transfer process is solvent dependent. Three main types of behavior have been observed and have been rationalized in terms of the possible solution species occurring in the various solvents. It has been proposed that (a) in nonpolar solvents, e.g., benzene, kinetically stable dimers are present, (b) in polar but not strongly coordinating solvents, e.g., acetone, a monomer–dimer equilibrium exists with a relatively rapid exchange rate, and (c) in strongly coordinating solvents, e.g., dimethyl sulfoxide, only solvated monomeric species are present. In order to obtain further information regarding the nature of the complex species in solution we have investigated the ^1H NMR spectra of the diamagnetic lutetium acetylacetonate complex, $Lu(acac)_3{\cdot}2H_2O$, in these solvents and report the results below. The possible implications of these results with respect to a previous interpretation[3] of the anomalous NMR spectrum of $Mg(acac)_2$

Table I. Molecular Weight Measurements of $Ln(acac)_3 \cdot 3H_2O$ in Benzene Solution[a] at 310 K

Ln	$\bar{n}^b$ (±0.15)	Ln	$\bar{n}^b$ (±0.15)
Pr	2.03	Dy	1.76
Nd	1.89	Ho	1.93
Sm	2.06	Er	1.87
Eu	2.03	Yb	1.67
Gd	2.12	Lu[c]	1.66
Tb	1.98		

[a] 0.01 M with respect to monomer. [b] $\bar{n}$ is the average number of monomers per solute molecule. [c] The dihydrate complex.

in $CDCl_3$ solution are also discussed.

Experimental Section

Preparation of Complexes. The complexes $Ln(aa)_3 \cdot 3H_2O$ where Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Yb were prepared by a standard method[4] and C and H analyses gave percent values within 0.3 of the theoretical figures. In the case of lutetium the same method gave the dihydrate. (Anal. Calcd: C, 35.44; H, 4.96. Found: C, 35.39; H, 4.92.) A Karl Fischer water determination indicated the presence of 1.8 ± 0.3 molecules of water per complex molecule. All complexes were stored in tightly stoppered containers.

Molecular Weight Measurements. These were made on freshly prepared solutions using a Mechrolab Model 301 A vapor pressure osmometer with a nonaqueous probe at 310 K. The instrument was calibrated using benzil solutions. The solvent benzene was dried and redistilled before use.

^{1}H NMR Measurements. All measurements, unless otherwise stated, were made on a 100-MHz Varian HA-100 spectrometer. All solvents were perdeuterated and were dried and stored over molecular sieves. A 3% internal TMS reference was used and resonances are quoted in ppm downfield from this reference. The 220-MHz spectrum was obtained at the Physical Chemistry Measurements Unit, Harwell, England.

Results and Discussion

The possible self-association of lanthanide tris(acetylacetonate) complexes in solution has been discussed by several workers. Biltz[5] reported some lanthanide acetylacetonates to be dimeric in nonpolar solvents. Freed et al.[6] later proposed that dimers occurred in benzene solutions of the europium complex and that a monomer–dimer equilibrium could exist. Moeller et al.,[7] in conflict with the previous results, reported that the complexes were monomeric in carbon tetrachloride and benzene solutions. Other results[8] have indicated the presence of a monomer in acetone and more complicated behavior in dioxane. Later Pope et al.,[4] who recognized the hydrated nature of these complexes, found that the trihydrates $Ln(acac)_3 \cdot 3H_2O$ in benzene gave apparent molecular weights between 500 and 700. We have made molecular weight determinations of 11 lanthanide acetylacetonate complexes in benzene solution at 310 K using vapor pressure osmometry (Table I) and the obtained values of $\bar{n}$ indicate that association occurs in all cases and suggest that the oligomeric species is a dimer. The decrease in $\bar{n}$ toward the end of the lanthanide series may be the result of incomplete dimerization or the loss of water from the dimeric species.

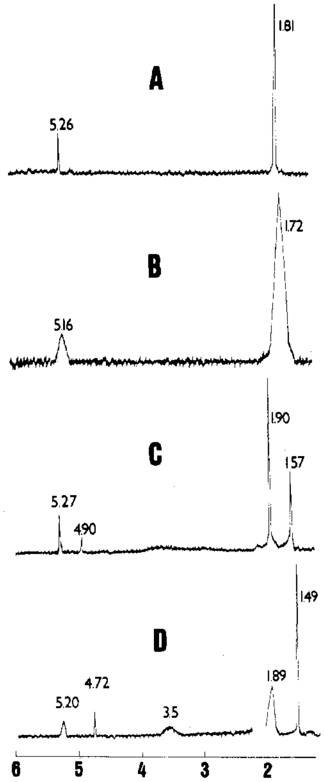

Figure 1. The 100-MHz NMR spectra (in ppm) of a 0.05 M solution of $Lu(acac)_3 \cdot 2H_2O$ in benzene-d_6 at 383 K (A), 343 K (B), and 278 K (C) and a 0.02 M solution of $Lu(acac)_3 \cdot 2H_2O$ in toluene-d_8 at 213 K (D). Resonances due to the solvent are omitted in spectrum D.

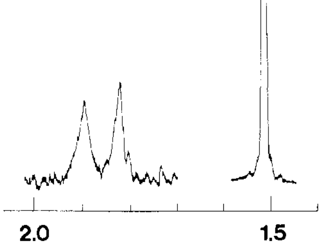

Figure 2. The 220-MHz ^{1}H NMR spectrum (in ppm) of $Lu(acac)_3 \cdot 2H_2O$ in toluene-d_8 solution at 203 K showing the ligand methyl resonances (ca. 0.01 M).

The ^{1}H NMR spectra of the diamagnetic complex $Lu(acac)_3 \cdot 2H_2O$ have been determined at ca. 10-K intervals in toluene over the temperature range 213–303 K and in benzene solution over the temperature range 278–383 K. Representative spectra are shown in Figure 1. At 278 K identical spectra are obtained in these solvents. The profiles of the spectra are temperature dependent and the resonance(s) in the region of 1.5–1.9 may be assigned to ligand methyl groups and the resonance(s) in the region 4.7–5.3 to the 3-H ligand proton (resonance values are quoted as ppm downfield from the internal TMS reference). These are in the expected 6:1 intensity ratio. Two separate methyl and 3-H resonances occur at temperatures below the coalescence temperature of ca. 343 K (Figure 1B). The ratios of the low-field:high-field components of these resonances were found to be 2:1 at all temperatures and also to be independent of concentration. These results suggest that the resonances are due to a single species which, on the basis of the molecular weight measurements, is probably a dimer. As the temperature is decreased toward 213 K, the low-field components of the resonances broaden (Figure 1D) but do not resolve. In view of this broadening the spectrum was measured using a 220-MHz spectrometer at 203 K. This spectrum shows a narrow high-field component at 1.51 but the low-field component is split into two equal-intensity broad resonances at 1.82 and 1.89 (Figure 2). The temperature dependence of the spectral

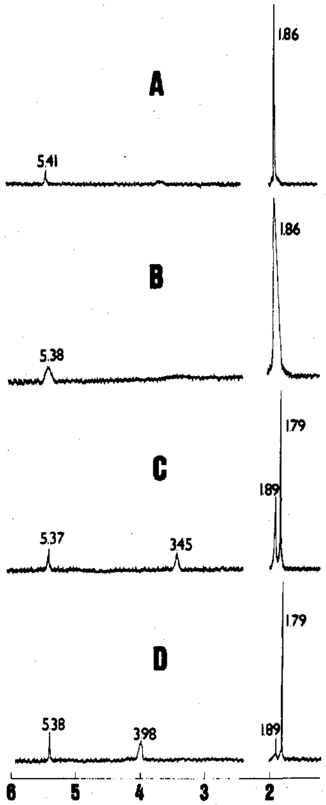

Figure 3. The 100-MHz NMR spectra (in ppm) of a 0.128 M solution of $Lu(acac)_3 \cdot 2H_2O$ in acetone-d_6 at (A) 363 K, (B) 303 K, (C) 273 K, and (D) 233 K. Resonances due to the solvent are omitted.

profiles indicates that two distinct types of intramolecular ligand exchange occur, one of which is relatively fast with a coalescence temperature below 213 K and the other of which is a slower type with a coalescence temperature of ca. 340 K, both relative to 100 MHz. Although the observed 2:1 and 1:1:1 ratios of the methyl resonances provide information about the inequivalences of the methyl groups, they do not allow any unambiguous assignment of structure to the complex particularly since the water molecules may have a possible bridging role. A broad resonance at ca. 3.5 was observed in the lower temperature toluene-d_8 solution spectra (Figure 1D) which is attributable to water on the basis of integration. The position of this resonance was temperature and concentration independent suggesting that the water molecules are exchanging between similar sites on the complex. Increasing the temperature above 343 K caused line narrowing typical of a fast-exchange region (Figure 1A).

The NMR spectra of the lutetium complex have also been determined in acetone solution over the temperature range 183–363 K (Figure 3). At 183 K single narrow resonances corresponding to methyl and 3-H ligand protons occur at 1.78 and 5.38, respectively. With increasing temperature additional resonances appear at 1.89 and ca. 5.40 which grow in intensity relative to the initial Me and 3-H resonances and coalesce with them at ca. 303 K. Further increase in temperature causes line narrowing. The temperature dependence of the relative areas of the methyl and 3-H components below 303 K is different from the behavior found in the nonpolar solvents and suggests that these resonances are due to the presence of two discrete species. If the 1.89 and 1.79 methyl resonances are attributed to monomeric and dimeric species, respectively, in equilibrium in the acetone solution, then the dimer formation constant, K, where $K = [\text{dimer}]/[\text{monomer}]^2$, may be obtained using the spectral integrals. The integrals of the methyl resonances have been measured over the range 233–293 K (the 3-H peaks are not sufficiently resolved to be useful) and values of K have been determined on this basis. The linearity of the $\ln K$ against $1/T$ plot supports the view that a monomer–dimer or stoichiometrically equivalent equilibrium is occurring. Further measurements at concentrations within the experimentally useful range of 0.04–0.14 M gave identical K values within experimental error. The least-squares regression line of the $\ln K$ against $1/T$ plot gives values of $\Delta H° = -28.2$ kJ mol^{-1} and $\Delta S° = -74.5$ J K^{-1} mol^{-1} for the equilibrium with standard errors of 1.5 kJ mol^{-1} and 4.5 J K^{-1} mol^{-1}, respectively. It is unlikely that the tetramethylsilane reference in the acetone solution and the use of concentration rather than activity terms are likely to lead to large errors in the derived enthalpy and entropy values. The water molecules of the complex give a single resonance the position of which is dependent on both concentration and temperature and shifts downfield with increasing temperature. This behavior suggests that the water molecules are rapidly exchanging between solvent and complex sites with probably the latter predominant at the lower temperatures. The coalescence point at 303 K (Figure 3B) can thus be assigned to an intermolecular exchange between monomers and dimers in contrast to the intramolecular ligand-exchange coalescences found with the nonpolar solvents. This difference implies that the ligand-exchange rate is considerably faster in the dimeric species in acetone solution than that in either benzene or toluene and suggests that the basic structures of the dimeric species in these solutions may be different. Molecular weight measurements have been reported[2] for samarium, europium, and terbium acetylacetonates in acetone at 310 K of $\bar{n} = 1.47 \pm 0.2$. The present investigations indicate a significantly lower $\bar{n}$ value at this temperature for the lutetium complex which may reflect a decreasing tendency for self-association with complexes of this smaller ion.

In both dimethyl-d_6 sulfoxide and pyridine solutions at 303 K single narrow resonances corresponding to methyl and 3-H protons occur at 1.78 and 5.33 and at 1.84 and 5.41, respectively. Addition of either of these solvents to acetone or benzene solutions of $Lu(acac)_3 \cdot 2H_2O$ causes line narrowing and the appearance of these characteristic resonances. This behavior indicates that in these strongly coordinating solvents the sole solution species is a solvated monomer.

The NMR results are therefore consistent with previous proposals regarding the possible mechanisms of intermolecular energy transfer and its dependence on the nature of the solvent. They also show that it is necessary to obtain data over a wide range of temperature with this type of system before it is possible to draw conclusions about the possible nature of the solution species since any multiplicity of resonances may arise from inter- and/or intramolecular exchange mechanisms. The other diamagnetic lanthanide acetylacetonate $La(acac)_3 \cdot 3H_2O$ is not sufficiently soluble in benzene, toluene, or acetone to allow determination of NMR spectra but preliminary investigations with $Y(acac)_3 \cdot 3H_2O$ have shown the presence of more than one methyl resonance in these solvents.

The occurrence of more than one methyl resonance in a simple acetylacetonate complex is unusual[9,10] but has been reported[11] in the case of $Mg(acac)_2$ in $CDCl_3$ solution where two resonances occur. Brittain[3] has proposed that these are due to the coexistence of square-planar and tetrahedral isomers in the solution. The implied stability of a D_{2h} configuration with the electropositive Mg^{2+} ion (and also with the Ba^{2+} and Ca^{2+} analogues) is however questionable in that it would require a considerable degree of covalence in the metal–oxygen bonds. Square-planar acetylacetonate complexes are only known to occur with metal ions (e.g., Cu^{2+}, Pd^{2+}, Pt^{2+})[12] where there are specific energetic advantages over the sterically favored tetrahedral configuration. These considerations and the results obtained with the lutetium complex suggest that 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.

References and Notes

(1) G. D. R. Napier, J. D. Neilson, and T. M. Shepherd, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1487 (1975).
(2) J. D. Neilson and T. M. Shepherd, *J. Chem. Soc., Faraday Trans. 2*, **72**, 557 (1976).
(3) H. G. Brittain, *Inorg. Chem.*, **14**, 2858 (1975).
(4) G. W. Pope, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **20**, 304 (1961).
(5) W. Biltz, *Justus Liebigs Ann. Chem.*, **331**, 334 (1904).
(6) S. Freed, S. I. Weissman, and F. E. Fortess, *J. Am. Chem. Soc.*, **63**, 1079 (1941).
(7) T. Moeller and W. F. Ulrich, *J. Inorg. Nucl. Chem.*, **2**, 164 (1956).
(8) N. K. Dutt and P. Bandyopadhyay, *Nature (London)*, **181**, 1682 (1958).
(9) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).
(10) J. A. S. Smith and J. D. Thwaites, *Discuss. Faraday Soc.*, **34**, 143 (1962).
(11) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).
(12) J. P. Fackler, Jr., *Prog. Inorg. Chem.*, **7**, 361 (1966).
(13) R. G. Linck and R. E. Sievers, *Inorg. Chem.*, **5**, 806 (1966).
(14) R. D. Shannon and C. I. Prewitt, *Acta Crystallogr., Sect. B*, **26**, 1076 (1970).
(15) D. P. Graddon, *Coord. Chem. Rev.*, **4**, 1 (1969).

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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