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Nitric Oxide Reactivity with Manganese Complexes Containing Linear Pentadentate Ligands

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Abstract: Manganese(II) and manganese(III) complexes incorporating linear pentadentate ligands derived from various salicylaldehydes and triamines have been allowed to react with nitric oxide. The extent of nitric oxide reactivity with the manganese(II) precursors is a function of both the substituent on the salicylaldehyde ring and the central nitrogen donor. Bulky groups on the central nitrogen donor and electron-donating substituents on the salicylaldehyde portion produce complexes which have little affinity for NO. For those manganese(II) complexes which react with NO, reduction to formally manganese(I) appears to occur and in several cases isolable materials of formula $[MnL(NO)]^0$ are produced where L = pentadentate ligand. All the corresponding manganese(III) complexes, $[MnLX]^0$, where X = I⁻, NO_2^-, and NCS⁻, readily react in a nonreversible manner with NO to yield ESR-active solutions characteristic of manganese(II). Magnetic susceptibility measurements on these solutions suggest that the manganese(II) is high spin.

Introduction

The reactivity of nitric oxide with iron and manganese porphyrin complexes shows a pronounced ligand and metal oxidation state dependence.[1] The interaction of nitric oxide with a few ferric hemoproteins is reported to be accompanied by the transfer of an electron from NO to the ferric heme iron. Reducibility was demonstrated to be easier with hemoglobin than myoglobin. Ferric cytochrome peroxidase and horseradish peroxidase were reported, however, to not be reduced by NO but instead formed low-spin iron(III) adducts. Nitric oxide, on the other hand, has been recently shown[2] to reversibly react with $Fe^{III}(TPP)Cl$ to form diamagnetic $Fe^{II}(TPP)(Cl)(NO)$ where TPP represents the tetraphenylporphyrinato dianionic ligand. Previous work[3] by other researchers had formulated

Table I. Analytical Data for Manganese(I) Nitrosyl Adducts

Compd	% C		% H		% N		% weight loss	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
[Mn(SALDPT)(NO)](CHCl₃)	46.4	46.4	4.3	4.4	10.4	10.4	25.8	27.5
[Mn(5-BrSALDPT)(NO)](CHCl₃)₀.₅	38.3	38.5	3.2	3.4	8.9	8.8	13.5	13.9
[Mn(5-NO₂SALDPT)(NO)](CHCl₃)	39.6	39.9	4.0	3.6	13.7	13.3	22.9	23.1
[Mn(5-NO₂SALMeDPT)(NO)](CHCl₃)	40.9	40.9	3.7	3.7	12.9	13.0	22.9	23.1

this nitrosyl complex as high spin. In a related and more recent study the reaction of Fe(TPP)Cl with nitric oxide in the presence of a hydroxylic solvent has been shown to yield a reduced nitrosyl iron porphyrin, Fe(TPP)NO.[4] X-ray structural analysis reveals a square-pyramidal coordination group with a bent Fe–N–O linkage. Ferrous hemoproteins have been shown to react reversibly with NO to form paramagnetic Fe^{II}–NO derivatives where the unpaired electron of NO is considerably delocalized over the complex rather than localized on the iron or NO.[5]

In contrast, neither manganese(III) peroxidases, manganese(III) hemoglobin, nor manganese(III) myoglobin reacts with nitric oxide,[1] whereas Mn^{III}(TPP)X reversibly forms low-spin 1:1 complexes of formula[6] Mn(TPP)(X)(NO) where X = Cl⁻, CN⁻, and $C_2H_3O_2^-$. Alternatively the manganese(II) compounds of these ligands yield formally low-spin Mn(I) nitrosyl materials in each case.[1,6]

In an effort to expand the scope of nitric oxide reactivity we have been studying the reaction of NO with a series of stereochemically quite different five- and six-coordinate manganese(II) and manganese(III) complexes. The primary ligand environment in these materials is a linear potentially pentadentate ligand system derived from various substituted salicylaldehydes and selected triamines which differ in the group attached to the central nitrogen. Descriptions of each complex along with the corresponding abbreviations are shown in structure I.

I
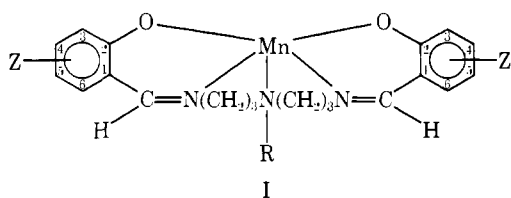
Mn(ZSALDPT), R = H; Z = H, 5-Br, 5-CH₃, 5-NO₂, 3-CH₃O
Mn(SALMeDPT), R = CH₃
Mn(SALPrDPT), R = C₃H₇
Mn(SALPhDPT), R = C₆H₅

Experimental Section

Materials. Nitric oxide was obtained from Matheson Gas Products, East Rutherford, N.J. All other chemicals and solvents were reagent grade or equivalent. Manganese(II) and manganese(III) complexes were synthesized by methods which have been previously described.[7,8]

Preparation of Manganese(I) Nitrosyl Complexes. A saturated CHCl₃ solution (100 mL) of the appropriate manganese(II) complex prepared in an inert atmosphere was exposed to a stream of nitric oxide for 2 h. Upon exposure to NO the slight red colored solution immediately turned dark blood-red followed by precipitation of a fluffy, red-purple material. After exposure to NO the flask was returned to the inert atmosphere box and the purple material was isolated via filtration, washed with CHCl₃, and dried in vacuo over CaCl₂ for 12 h.

Solution Preparation of Manganese(II) Nitrosyl Complexes. Nitric oxide complexes were formed by exposing a *N,N'*-dimethylformamide (DMF) solution of the appropriate manganese(III) complex to a bubbling stream of nitric oxide. The solution changed from green to yellow upon exposure to NO gas. Frozen and fluid ESR spectra were obtained on a 50/50 (v/v) mixture of DMF and toluene which had been thoroughly degassed with dry N₂ or Ar.

Instrumentation. Infrared absorption spectra in the region 4000–250 cm⁻¹ were obtained employing Nujol mulls with a Beckman IR-20A recording spectrophotometer. Magnetic susceptibility data were obtained at room temperature by the Faraday method using mercury(II) tetrathiocyanatatocobaltate(II) as the calibrant. Diamagnetic corrections were made employing Pascal's constants. Solution magnetic susceptibility measurements were performed by the NMR method.[9] Ultraviolet–visible spectra were obtained in solution with a Hitachi Model 100-60 spectrophotometer. Thermal gravimetric analyses (tga) in the temperature range 25–200 °C were performed using a Stone Model 5 instrument. Samples were run in vacuo with a temperature programming rate of 5 °C/min with weight losses being detected by a Cahn RG electrobalance. Elemental analysis were performed by the Analytical Services Division of the Chemistry Department of Virginia Polytechnic Institute and State University on a Perkin-Elmer 240 carbon–hydrogen–nitrogen analyzer. The electron spin resonance data were obtained on a Varian E-12 ESR instrument which contained an X-band E-101 microwave bridge.

Results and Discussion

Bright, fluffy, purple-red materials are isolated when CHCl₃ solutions of Mn^{II}(ZSALDPT), Z = H, 5-Br, and 5-NO₂, are exposed to a stream of nitric oxide. In those cases where Z = 3-CH₃O and 5-CH₃, purple-red materials formed which were reminiscent of the other derivatives; however, NO was lost during isolation leaving behind a bright yellow solid whose infrared spectrum was superimposable on that of the starting material. The three isolable nitrosyls were found to be stable at room temperature in air for approximately 1 month. They readily dissolve in chloroform, benzene, methylene chloride, and toluene to give red solutions which immediately darken on exposure to air. Analytical results (Table I) support the incorporation of one nitric oxide moiety and one solvent molecule of crystallization per manganese. Infrared spectra lend further evidence to this assignment. Bands at 1715 cm⁻¹ due to coordinated NO and at 1210 and 750 cm⁻¹ due to CHCl₃ are observed in each nitrosyl complex but these bands are absent in the starting material (Figure 1). The N–O stretching frequency at 1715 cm⁻¹ is similar to that observed in the $[Mn^I(CN)_5(NO)]^{3-}$ complex at 1725 cm⁻¹.[10] The constant position of the N–O stretch in all these nitrosyl complexes suggests that the coordination of NO in each case must be nearly the same. Coupled with the NO coordination there is a shift (~30 cm⁻¹) in the N–H stretch to higher energy which is consistent with an increase in electron density at the manganese site which could arise from a lower formal manganese oxidation state and/or an increase in manganese coordination number.

The loss of NO and CHCl₃ on heating (~100 °C, in vacuo) occurs readily in each case as revealed by tga analysis (Table I). No evidence for a two-step-weight loss exists corresponding to the removal of one NO followed by CHCl₃ or vice versa (Figure 2). Apparently NO and CHCl₃ are lost without decomposition of the complex because if the nitrosyl adducts of Mn(SALDPT) and Mn(5-BrSALDPT) are heated in vacuo for 3 h at 78 °C, each purple material is converted into a bright yellow one reminiscent of the manganese(II) precursor. As evidence for this assignment magnetic susceptibility data, infrared, and ESR spectra of manganese(II) precursor and yellow material from the tga experiment are superimposable. Examination of the material after thermal gravimetric analysis
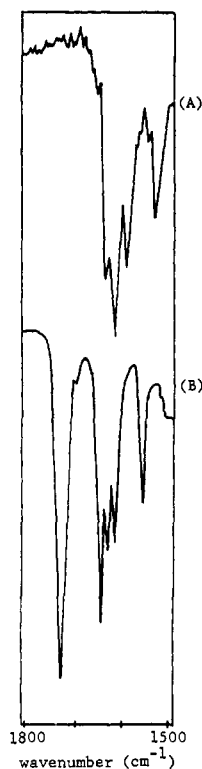
Figure 1. Infrared spectra of (A) Mn(SALDPT) and (B) [Mn(SALDPT)NO]·CHCl₃.

Figure 2. Thermal gravimetric analysis of [Mn(SALDPT)NO]·CHCl₃, scan rate = 2 °C/min.

of [Mn^I(5-NO$_2$SALDPT)(NO)](CHCl$_3$) suggests that some sample decomposition occurs under these conditions.

Magnetic susceptibility data for the isolable nitrosyl adducts were taken at room temperature in the solid state. Each complex is diamagnetic ($\mu_{eff} < 0.2$ μ_B). No ESR signal was observed during measurements on the freshly prepared complexes in agreement with similar studies on manganese(II) porphyrins.[1] Weak signals, however, begin to appear with complexes as little as 1 week old, which lends credence to the idea that these nitrosyls are susceptible to slow decomposition when exposed to air in the solid state. It is therefore suggested that based on the infrared and magnetic evidence these nitrosyl complexes are correctly formulated as Mn^I-(NO$^+$) wherein the formally manganese(I) is low spin.

Reactions with NO were also carried out on Mn^{II}(ZSAL-MeDPT) where Z = H, 5-Br, and 5-NO$_2$ under the same conditions employed with Mn(ZSALDPT). Upon exposure to NO, solutions of the manganese(II) complexes turned dark red with the disappearance of an ESR signal. All attempts to isolate a nitrosyl adduct of Mn(SALMeDPT) were unsuccessful owing to the fact that the dark red adduct readily reverted to the yellow precursor upon filtration. Isolation of the bright red nitrosyl complex of Mn(5-BrSALMeDPT) in an inert atmosphere facility was followed by a slow but clearly visible loss of NO. The nature of the brown compound produced when this NO is removed is uncertain. Infrared spectra as a function of time confirmed this NO loss and suggested a rather labile Mn-NO bond (Figure 3). Only in the 5-NO$_2$ case was an air-stable nitrosyl complex isolated. Elemental analyses and tga data (Table I) support the formulation [Mn^I(5-NO$_2$SALMeDPT)(NO)](CHCl$_3$). An NO stretch at 1715 cm^{-1} and a magnetic moment of 0.09 μ_B are in keeping with the results obtained on the analogous [Mn^I(ZSALDPT)-(NO)](CHCl$_3$). Loss of NO on heating again yielded the manganese(II) precursor.

These results suggest that the electron density about the manganese(II) is very critical and conditions must be precise
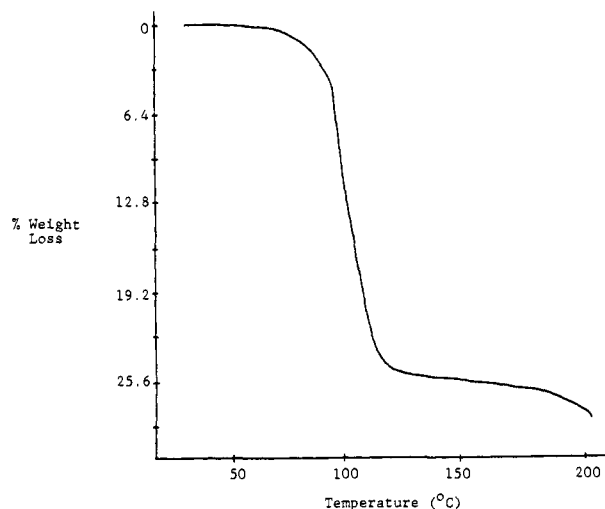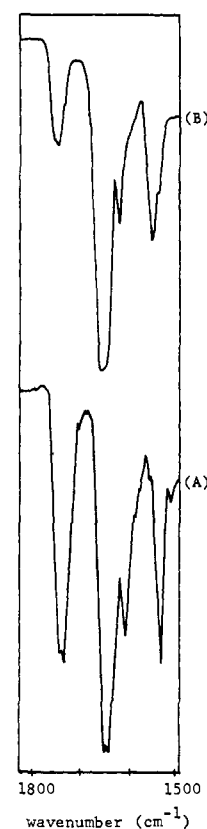

Figure 3. Infrared spectra of (A) [Mn5-BrSALMeDPT)NO] prepared in an inert atmosphere and (B) [Mn(5-BrSALMeDPT)NO] exposed to air for 0.5 h.

before a nonlabile bond will form between Mn and NO. For example, those complexes that possess ligands which increase electron density on manganese render less stable Mn-NO links than vice versa. In an analogous fashion Mn(SALMeDPT), which possesses a better central electron donor in the N-CH$_3$ group compared to the N-H group, does not form a stable NO adduct. The introduction of electron-withdrawing groups on the salicylaldehyde portion of ZSALMeDPT, however, yields a very labile [Mn^I(5-BrSALMeDPT)(NO)] and a relatively stable [Mn^I(5-NO$_2$SALMeDPT)(NO)] complex. These trends are again consistent with the idea that electron-withdrawing substituents help stabilize the increased electron density on the manganese arising from NO coordination.

Table II. Analytical Data for Mn(SALDPT)(NO₂)

Complex	μ_{eff}, μ_B	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
[Mn(SALDPT)(NO₂)](H₂O)[a]	4.88	52.6	52.5	5.5	5.5	12.3	12.3
[Mn(SALDPT)(NO₂)](H₂O)₂[b]	4.99	50.6	50.6	5.7	5.6	11.8	11.8
Mn(SALDPT)(NO₂)[c]	4.83	54.8	54.7	5.3	5.3	12.8	13.1

[a] Prepared by reacting MnL(NO) in the solid state with O₂. [b] Prepared by reacting MnL(NO) in CHCl₃ solution with O₂. [c] Prepared by reacting MnL with O₂ in the presence of NO₂⁻.
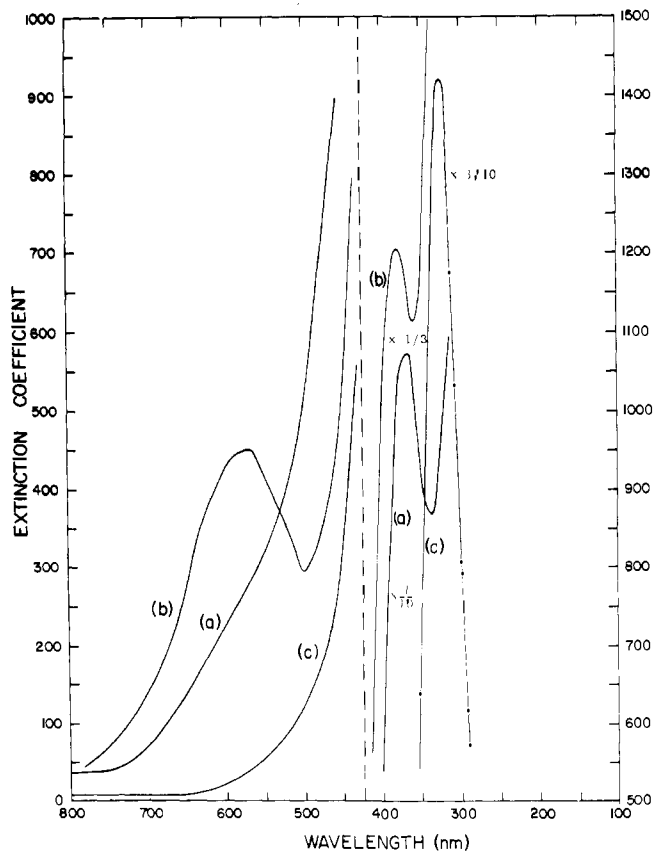

Figure 4. Ultraviolet–visible spectra of (a) Mn(SALDPT), (b) [Mn(SALDPT)(NCS)], and (c) [Mn(SALDPT)(NCS)] + NO in DMF.

Figure 5. ESR spectrum of [Mn(SALDPT)(NCS)] + NO in degassed DMF–toluene, 50/50 (v/v) at 296 K.

The substituent attached to the central nitrogen donor also influences the reactivity of these pentadentate ligand containing complexes with NO. For example, no reaction is observed with either Mn(SALPrDPT) or Mn(SALPhDPT) when CHCl₃ solutions of each are exposed to NO, whereas Mn(ZSALDPT) and Mn(ZSALMeDPT) have been stated to readily react with NO. The reason for the failure of these materials to react with NO is not entirely clear. Stereomodels of Mn(SALPrDPT) based on the x-ray structural determination of Ni(SALMeDPT)[11] reveal that the propyl group should offer considerable steric hindrance at the anticipated point of attack (i.e., cis to *N*-propyl rather than trans to *N*-propyl) by NO. This hypothesis is based on the assumption that the point of attack by NO should be the same as that observed in the reaction of dioxygen with Co(SALDPT) and Co(S-ALMeDPT).[12] An x-ray structural analysis[13] has substantiated that the dioxygen occupies the position cis to *N*-methyl. Mn(SALPhDPT) presents somewhat similar steric restraints in addition to its having a weaker central donor than Mn(SALPrDPT). The hydrogen substituent of DPT does not block the cis position thereby allowing electronic effects to become dominant in this case. An analogous reactivity pattern has recently been observed[7] with dioxygen for this series of
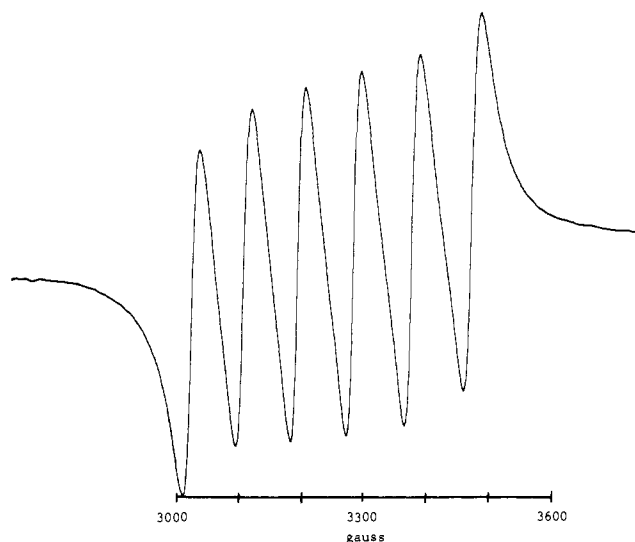
manganese(II) compounds in that propyl- and phenyl-substituted central donors exhibited very little affinity for dioxygen while ZSALDPT and ZSALMeDPT type ligands rapidly reacted.

As mentioned previously several of these nitrosyls have a tendency to lose NO in the solid state thereby regenerating the manganese(II) precursor. One derivative, however, renders the coordinated nitrosyl susceptible to oxidation. Over a period of 6 months red-purple [Mnᴵ(SALDPT)(NO)](CHCl₃) slowly changes to a green material. During this time the previously cited N–O stretch in the complex at 1715 cm⁻¹ gradually disappears, a broad band attributable to H₂O appears around 3400 cm⁻¹, and the magnetic moment per manganese increases to 4.88 μ_B. Elemental analysis data support the formulation of the green material as [Mnᴵᴵᴵ(SALDPT)(NO₂)]-(H₂O) (Table II). An identical compound can be prepared in a much shorter time period by bubbling O₂ into a CHCl₃ solution of [Mnᴵ(SALDPT)(NO)]CHCl₃. Immediately upon addition of O₂ the solution turns green followed by precipitation of a green solid. Long green needles of this product can be prepared by allowing a saturated CHCl₃ solution of [Mnᴵ-(SALDPT)(NO)]CHCl₃ to stand in the air overnight. Pertinent analytical data for this product are shown in Table II which is again in agreement with a Mn³⁺–(NO₂⁻) assignment. Examination of the other isolable nitrosyls in chloroform solution revealed that they too are air oxidized in this manner. As further proof that this oxidized product was of the type Mn³⁺–(NO₂⁻), a third method of preparation was devised based on a recent report[14] which described the synthesis of a series of manganese(III) complexes by aerating a solution of manganese(II) complex in the presence of an appropriate anion. By an analogous route we have prepared Mn(SALDPT)(NO₂) (Table II). This material is identical in all respects with the two materials prepared by oxidation of the nitrosyl complex except for the absence of infrared bands at-

Table III. ESR Parameters of Reaction Product of Mn(III) Complexes with NO

Compd	g_{eff} fluid	Coupling fluid, G	g_{eff} frozen	Coupling frozen, G
Mn(SALDPT)(I)	2.006	90.0	1.991	86.7
			1.977	88.3
			2.017	91.0
Mn(SALMeDPT)(I)	2.005	90.0	1.985	86.7
			1.972	90.0
			2.011	90.0
Mn(SALPrDPT)(I)	2.006	90.0	1.985	88.3
			1.972	90.0
			2.012	90.4
Mn(SALPhDPT)(I)	2.006	90.0	1.985	88.3
			1.961	90.0
			2.009	90.0
Mn(SALDPT)(NO₂)	2.005	90.0	1.979	90.0
			1.965	92.0
			2.002	88.0
Mn(SALDPT)(NCS)	2.007	90.0	1.979	90.0
			1.966	92.0
			2.003	88.0
Mn(5-CH₃SALDPT)(I)	2.014	90.0	1.982	93.0
			1.972	92.0
			2.008	88.0
Mn(5-CH₃SALDPT)(NCS)	2.018	90.0	Unresolved	
Mn(5-ClSALDPT)(NCS)	2.002	88.9	1.990	95.0
			1.974	95.0
			2.012	88.0
Mn(5-NO₂SALDPT)(NCS)	2.011	89.0	1.996	92.0
			1.980	91.0
			2.081	89.0

Figure 6. ESR spectrum of [Mn(SALDPT()NCS)] + NO in degassed DMF–toluene, 50/50 (v/v) at 120 K.

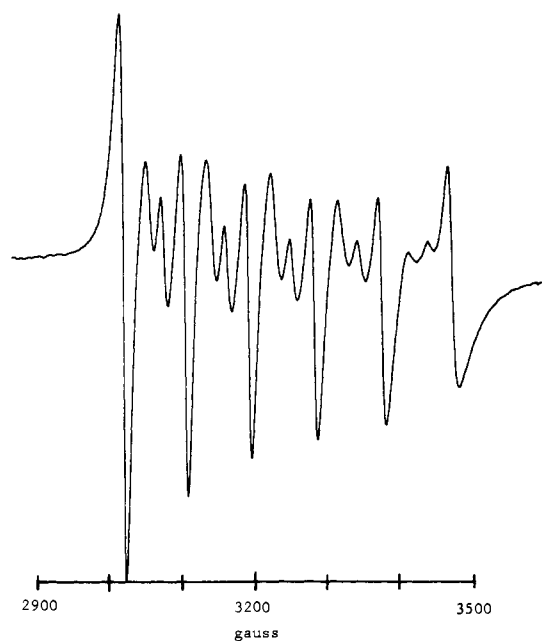Figure 7. ESR spectrum of Mn(SALDPT) in deoxygenated DMF–toluene, 50/50 (v/v) at 120 K.

tributable to an O–H stretch arising from water of hydration. Efforts to unequivocally locate the vibrational modes of nitrite ion in these three preparations were hampered by numerous ligand absorptions in the 1400–1000-cm⁻¹ region.

Manganese(III) Complexes. The propensity of these pentadentate ligands to promote reaction with nitric oxide is more apparent with manganese in the +3 oxidation state. For example, unlike the divalent case, Mn(SALPrDPT)Y and Mn(SALPhDPT)Y readily react with NO. In addition, the extent of reaction with NO appears to be complete and insensitive to changes in the anion or salicylaldehyde substituent.
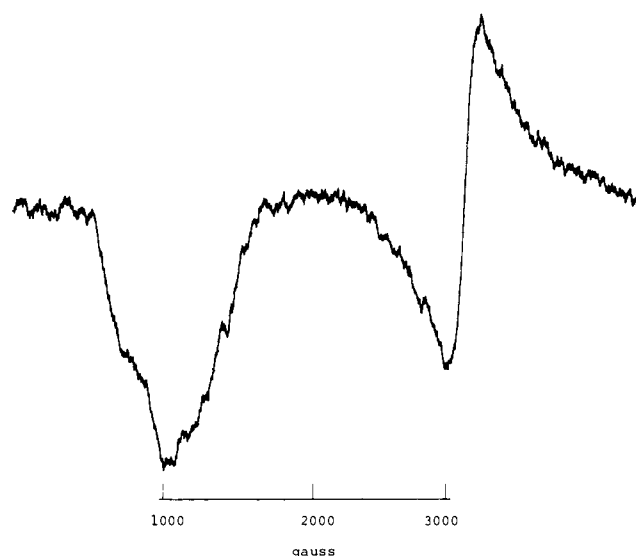
Numerous attempts to isolate nitrosyl adducts from reactions with Mn(ZSALRDPT)Y, where Y equals I⁻, NCS⁻, and NO₂⁻, in DMF or CH₂Cl₂ were unsuccessful. Ultraviolet-visible and ESR spectroscopy, however, conclusively prove that reaction with NO occurs under these reaction conditions. A major color change from green to yellow is observed in each exhaustively deaerated Mn(III) solution (DMF, CH₂Cl₂, Me₂SO) upon exposure to NO. Typical spectral changes before and after reaction with NO are illustrated in Figure 4. Special note would be taken of the broad band at ca. 600 nm in the manganese(III) complex which disappears on exposure of the solution to NO. The band is attributable to a d–d transition and its elimination from the spectrum no doubt signals the reduction of Mn(III). Equally significant changes take place in the

ESR spectrum of these solutions. While the precursor is ESR silent, an intense six-line pattern develops in the corresponding ESR spectrum (Figures 5 and 6) of the fluid and frozen solution of the NO reaction product. The six lines arise from the interaction of the unpaired electrons and the manganese nucleus ($I = \frac{5}{2}$).[5] The narrowest line has a width of 11 G and shows no hint of super-hyperfine structure due to electron spin interaction with the nitrogen of the nitrosyl ligand. A weak ESR signal is also observed at $g_{eff} \sim 4.2$ (1565 G) for each derivative. Degassing these solutions with N_2 or prolonged evacuation does not generate loss of the ESR signal.

The magnitude of the manganese hyperfine coupling constants of approximately 90 G (Table III) and the absence of ^{14}N splitting strongly suggest that there is complete transfer of the odd electron on NO to manganese(III). If the odd electron were principally localized on the nitrosyl nitrogen the ^{14}N coupling constant would be expected to be on the order of 31–35 G.[15,16] These measured coupling constants show no ligand dependence and differ very little from those observed in high- and low-spin manganese(II) complexes (e.g., $[Mn(TPP)(NO)(CN)]^0$ (88.2 G),[17] $[Mn(CN)_5(NO)]^{2-}$ (77.4 G),[18] and $[Mn(H_2O)_6]^{2+}$ (95.0 G)).[18] Therefore, an assignment of spin state is not possible based on this information. The presence of the signal at $g_{eff} \sim 4.2$, while less intense, is, nevertheless, compatible with other known manganese(II) high-spin complexes.[19,20] Additional support beyond ESR data for formulation of the species in solution as high-spin Mn(II) was obtained via magnetic susceptibility measurements on DMF solutions previously exposed to NO that had been thoroughly degassed with a stream of argon. Each sample assuming a formulation of $[Mn(ZSALDPT)NO]Y$ yielded a magnetic moment between 5.9 and 6.1 μ_B, which is consistent with known high-spin manganese(II) complexes.[21] These results are in contrast to the results obtained when $Mn^{III}(TPP)Y$ (Y = Cl^-, CN^-) was treated with NO.[2] This complex yielded an ESR that was stated to arise from a low-spin Mn(II) complex, although no magnetic susceptibility measurement could be made because of the extreme reversibility of this system.

While the fate of NO in its reaction with manganese(II) is coordination to Mn(I), the fate of NO reacting with manganese(III) is not entirely clear. Reduction of $Mn(ZSALRDPT)Y$ to $Mn(ZSALRDPT)$ apparently does not occur since UV–visible and ESR spectra of an NO reacted solution and a $Mn(ZSALRDPT)$ solution prepared via an independent route are significantly different (Figures 4–7). This conclusion is supported by the observation that NO reacted solutions are quite stable to oxygen, whereas $Mn(ZSALRDPT)$ rapidly discolors in air. Coordination of NO to yield $[Mn(ZSALRDPT)NO]Y$ is an obvious alternative; however, no N–O vibrational mode can be discerned in the infrared spectrum of a thoroughly degassed solution. In light of the striking similarity between the ESR spectra of $[Mn(TPP)(NO)Y]$ and our NO reaction product it is highly conceivable, we believe, that the species in solution is $[Mn(ZSALRDPT)(NO)Y$. Alternatively, differences in conformation of the pentadentate ligand in the NO reacted species and $Mn(ZSALRDPT)$ could account for these spectral and reactivity changes.

It has been advanced that an increased g_{eff} value above that of a free electron is due in part to greater covalency in the metal–ligand bond.[22] An examination of Table III shows that an electron-donating substituent ($5\text{-}CH_3$) gives rise to higher g_{eff} values than the unsubstituted products; therefore, a higher degree of covalency is anticipated. Some support for this idea comes from the $Mn(5\text{-}CH_3\text{-}SALDPT)(SCN)$ case, where the splitting in frozen solution is unresolved tending to indicate more electron delocalization between Mn and NO.

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