while M–S bonds trans to oxo ligands generally fall in the range of 2.6–2.7 Å.[35] Furthermore, the isolation of stable five-coordinate oxomolybdenum(IV)–dithiocarbamate complexes, $OMo(S_2CNR_2)_2$,[10,11] provides literature precedent for the putative $OW(S_2CNR_2)(R^1C_2R^2)(SC(=S)NR_2)$ intermediate. Following formation of the intermediate, the ensuing ligand rearrangement could take place along one of several plausible pathways, the only requirement being that all four alkyl groups on the two bidentate ligands must eventually exchange with one another. The general reticence of octahedral metal complexes to isomerize without bond cleavage,[36] the high trans influence of the oxo ligand, the stability of five-coordinate group 6 oxo species, and the propensity of five-coordinate complexes to undergo facile intramolecular rearrangements[37] merge to offer a plausible molecular explanation for the dynamic behavior of these complexes in solution.

Acknowledgment. Purchase of the inert-atmosphere box used in these studies was made possible by a Cottrell Research Grant from Research Corp. J.L.T. gratefully acknowledges the donors of the Petroleum Research Fund, as administered by the American Chemical Society, for partial support of this work.

Registry No. **1**, 76429-48-6; **2**, 76429-49-7; **3**, 76429-50-0; **4**, 73367-39-2; $Mo_2O_3[S_2P(OEt)_2]_4$, 27862-11-9; $W(CO)(C_2H_2)(S_2CNEt_2)_2$, 66060-14-8; $W(CO)(C_2H_2)(S_2CNMe_2)_2$, 76429-51-1; $W(CO)(PhC_2H)(S_2CNMe_2)_2$, 73848-24-5; $Mo(CO)(DTA)(S_2CNEt_2)_2$, 76429-52-2.

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Characterization and Electrochemistry of Manganese(III) Complexes Containing Pentadentate Ligands

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Manganese(III) complexes incorporating linear potentially pentadentate Schiff base ligands have been prepared from their manganese(II) precursors. Magnetic susceptibility, visible spectra, and conductivity measurements suggest the manganese(III) ion is in a pseudooctahedral environment. The reduction potentials of the Mn(III)/Mn(II) couple as measured by cyclic voltammetry show a dependence upon the donor atom set as well as an aromatic ring substituent effect. The electrochemistry of complexes containing potential hexadentate ligands is also discussed. Several complexes wherein one of the ligand donor groups may be dangling exhibit a unique ligand oxidative wave.

Introduction

In the last few years, we have been concerned with the reaction of small molecules such as O_2 and NO with manganese complexes which may mimic certain biological processes. One of the most widely studied group of compounds in this regard is the Mn(II) and Mn(III) complexes of Schiff base ligands derived from a substituted salicylaldehyde (ZSAL) and dipropyltriamine (DPT). Differences in chemical reactivity of the Mn(II) compounds toward O_2 have been observed and attributed in part to the Z component on the SAL ring.[1] If Z is an electron-withdrawing group, oxygenation is relatively slow and stops at an O_2:Mn ratio of 0.5. If Z is an electron-donating group, continued oxidation of the complex (presumably the ligand itself) occurs. Reaction of Mn(II) with NO results in a reduction to Mn(I).[2] the resulting reversible NO adducts were found to be most stable with electron-withdrawing substituents on the SAL portion of the Ligand.

Electronic effects no doubt account in part for these reactivity patterns. Manganese(III) complexes of SALDPT and its derivatives have been studied[3] via electrochemical techniques, and it was observed that the Mn(III)/Mn(II) reduction is clearly related to the Z component on the SAL portion of the ligand. Electron-withdrawing groups make the Mn(III)/Mn(II) reduction easier while the electron-donating groups make it more difficult. We have now expanded our electrochemical studies to other systems and report some of these results herein.

The pentadentate ligand modifications include the number of carbon atoms in the amine portion of the ligand and substituents on the salicylaldehyde ring (structure I). We have also studied the electrochemistry of four similar complexes previously reported[4] which contain potential hexadentate ligands (structure II).

Experimental Section

Materials. Salicylaldehyde (SAL) was obtained from Fisher Scientific Co. 5-Nitrosalicylaldehyde and 3-nitrosalicylaldehyde were obtained from Eastman Chemical Co. Bis(3-aminopropyl) ether (DAPE) was prepared by a catalytic hydrogenation similar to that reported previously.[5] *N*-(2-Aminoethyl)-1,3-propanediamine (EPT) and *N*-(3-aminopropyl)-1,4-butanediamine were obtained from Aldrich Chemical Co. All other chemicals and solvents were reagent grade or equivalent.

Synthesis of the Complexes. The following is a general method for the preparation of all of the complexes cited here. To a 30-mL

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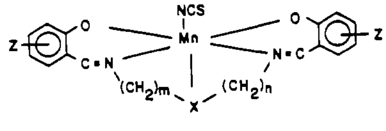
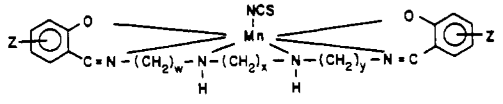


I

m	n	x	Name
2	3	N-H	ZSALEPT
3	4	N-H	ZSALBPT
3	3	N-H	ZSALDPT
3	3	O	ZSALDAPE

Z = H, 3-NO_2, 5-NO_2, 5-CH_3O



II

w	x	y	Name
2	2	2	SAL-1,4,7,10
3	2	3	SAL-1,5,8,12
3	3	3	SAL-1,5,9,13

Z = H, 5-NO_2

tert-butyl alcohol solution containing 0.02 mol of aldehyde was added 0.01 mol of the appropriate amine. This yellow solution was refluxed under N_2 for 10 min after which 0.02 mol of KOH dissolved in 10 mL of O_2-free H_2O was added. An additional 5 min of refluxing was followed by the dropwise addition of 0.01 mol of $Mn(C_2H_3O_2)_2{\cdot}4H_2O$ dissolved in 20 mL of O_2-free CH_3OH. The resulting solution was refluxed for $^1/_2$ h followed by the addition of excess NH_4NCS (0.05 mol) as a solid. The heat was removed, and while the solution was still warm, dry O_2 was bubbled through the solution, resulting in a color change from orange to green or dark brown. Depending on the complex, precipitation either occurred when the solution reached room temperature or occurred overnight. The material was isolated via suction filtration, washed with alcohol, and dried over anhydrous $CaCl_2$ in vacuo overnight.

Physical Measurements. Elemental analyses were preformed with use of a Perkin-Elmer Model 240 C, H, and N analyzer or obtained commercially. Infrared spectra were obtained with a Beckman 20AX recording spectrophotometer as Nujol mulls. Visible–UV spectra were recorded in Me_2SO and in the solid state with use of a Hitachi Model 100-60 spectrophotometer. Magnetic susceptibility data were obtained by the Faraday method at room temperature and at several different magnetic fields using $Hg[Co(SCN)_4]$ and $Ni(en)_3S_2O_3$ as the calibrant. Diamagnetic corrections were made by employing Pascal's constants. Conductivity measurements were made on an apparatus described previously.[6] All electrochemical studies were carried out in Me_2SO with tetraethylammonium perchlorate as the supporting electrolyte, a Pt electrode as the working electrode, and an SCE which was separated from the Me_2SO solution by means of a salt bridge as the reference electrode. Measurements were made with the instrumentation described previously.[3]

Results and Discussion

Manganese(III) complexes of potentially pentadentate ligands with the donor sets N_3O_2 and N_2O_3 and potentially hexadentate ligands with the donor set N_4O_2 have been synthesized. Data for the complexes with pentadentate ligands are given in Tables I and II and indicate the general formula $Mn^{III}(L)NCS$. The hexadentate ligands have been previously reported,[4] and the same general formula is found. In the solid state and in solution, all Mn(III) complexes appear to be quite stable.

The proposed formulation for the pentadentate compounds is supported by infrared data. Those complexes formulated as hydrates have broad bands around 3400 cm^{-1} which are assigned to OH stretching modes. The infrared spectra of all compounds display a strong absorption band in the region 1650–1610 cm^{-1} which is assigned to a C=N stretching mode in the Schiff base. All complexes also show the characteristic C≡N stretch for an N-coordinated thiocyanate ion around 2050 cm^{-1}.[7] The C—O—C stretching frequency for the ZSALDAPE complexes occurs at 1080 cm^{-1} compared with 1110 cm^{-1} for the free ligand.[8] This observation suggests that the ether oxygen is only slightly coordinated to Mn(III). A much larger shift to lower energy (65 cm^{-1}) occurs in the complex $[Ni(DAPE)_2]X_2$ in which the oxygen is coordinated.[9]

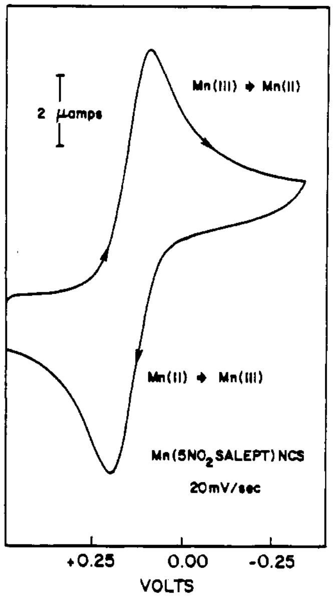


Figure 1. Cyclic voltammogram of $Mn(5\text{-}NO_2SALEPT)NCS$ in dimethyl sulfoxide. Scan rate = 20 mV/s.

The experimental magnetic moment for each manganese complex is listed in Table I. The values are near those for known high-spin d^4 complexes supporting the formulation as Mn(III).[6] Conductivity measurements in dimethyl sulfoxide (Me_2SO) are in the range expected for 1:1 electrolytes[10] (Table II) (40–50 cm^2 Ω^{-1} mol^{-1}).

Visible–UV electronic spectra of the complexes in Me_2SO and as Nujol mulls are presented in Table II and are consistent with a d^4 Mn(III) ion in an octahedral environment.[6,7,11] In the solid state, NCS^- occupies the sixth coordinating position but is replaced by a Me_2SO molecule in solution. Bands in the 500–600-nm region are assigned to d–d transitions. In the solid state these are normally observed, while in solution intense charge-transfer and intraligand bands sometimes obscure the weaker d–d bands. In most cases the solid-state and solution spectra appear to be quite different. There are also pronounced differences in the 5-NO_2, 3-NO_2, and unsubstituted derivatives. The lack of a well-resolved d–d band for all spectra makes it impossible to correlate any trend in this band position with the Z component.

Each complex readily undergoes an apparent one-electron reduction and subsequent reoxidation on sweeping anodically in the +0.3 to −0.3 V range. While both cathodic and anodic peak potentials (E_{pc} and E_{pa}, respectively) naturally differ, the behavior is analogous to previously reported data regarding other manganese(III) complexes wherein the reduction was attributed to Mn(III) → Mn(II).[3] The electrochemical properties of the complexes are those of a quasi-reversible redox couple (Table III) as indicated by (1) the E_{pc} and E_{pa}

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Table I. Elemental Analyses and Magnetic Moments of the Complexes

complex	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N	μ, μ_B
Mn(5-NO_2SALEPT)NCS·$^1/_2H_2O$	44.9	3.8	15.7	45.1	3.8	15.1	4.69
Mn(3-NO_2SALEPT)NCS·$^1/_2H_2O$	44.9	3.8	15.7	44.6	4.0	15.4	4.74
Mn(SALEPT)NCS·H_2O	52.9	5.1	12.3	52.5	4.7	12.3	5.02
Mn(5-NO_2SALBPT)NCS	47.7	4.2	15.1	47.8	4.2	14.6	4.82
Mn(3-NO_2SALBPT)NCS·H_2O	46.2	4.4	14.7	46.0	4.2	14.4	5.00
Mn(SALBPT)NCS·$^1/_2H_2O$	56.7	5.6	12.0	56.4	5.7	12.0	4.76
Mn(5-CH_3OSALBPT)NCS·H_2O	53.3	5.4	10.4	53.4	5.3	10.4	5.15
Mn(3-NO_2SALDAPE)NCS·$2H_2O$	43.7	4.2	12.1	44.2	3.8	11.7	5.01
Mn(SALDAPE)NCS	55.9	4.9	9.3	55.9	4.9	9.3	4.88
Mn(SALHTDA)NCS·$^1/_2H_2O$	58.8	5.4	9.4	58.7	5.4	9.3	4.91

Table II. UV-Visible Spectral Data and Molar Conductivity of the Complexes

complex	medium	λ,[b] nm	Λ_m[a]
Mn(5-NO_2SALEPT)NCS·$^1/_2H_2O$	solid	550 sh, 470 sh, 360, 270 sh	39
	Me_2SO	375 (30 000), 352 sh (23 800), 270 sh (22 500)	
Mn(3-NO_2SALEPT)NCS·$^1/_2H_2O$	solid	460, 360 sh, 265	36
	Me_2SO	440 sh (5800), 393 (8100), 355 sh (6300)	
Mn(SALEPT)NCS·H_2O	solid	630 sh, 500 sh, 355 sh, 290 sh	37
	Me_2SO	620 sh (255), 380 sh (5800), 270 sh (17 500)	
Mn(5-NO_2SALBPT)NCS	solid	560 sh, 375, 230	41
	Me_2SO	430 sh (7200), 355 (29 600), 270 sh (24 800)	
Mn(3-NO_2SALBPT)NCS·H_2O	solid	560 sh, 360 sh, 260 sh	39
	Me_2SO	550 sh (980), 385 (12 000), 265 sh (27 000)	
Mn(SALBPT)NCS·$^1/_2H_2O$	solid	570 sh, 370 sh, 260 sh	39
	Me_2SO	570 (485), 375 sh (5150), 280 (19 500)	
Mn(5-CH_3OSALBPT)NCS·H_2O	Me_2SO	605 (620), 400 sh (5900), 345 sh (8200), 285 (19 400)	27
Mn(3-NO_2SALDAPE)NCS·H_2O	solid	575 sh, 450 sh, 380 sh, 270	26
	Me_2SO	485 sh (4000), 419 (9400)	
Mn(SALDAPE)NCS	solid	585, 450 sh, 375, 275	36
	Me_2SO	590 (550), 380 (5800), 273 (27 300)	
Mn(SALHTDA)NCS	Me_2SO	585 sh (300), 360 sh (7200)	44

[a] In Me_2SO at 10^{-3} M. [b] Values in parentheses are the molar absorptivities (ε); sh stands for shoulder.

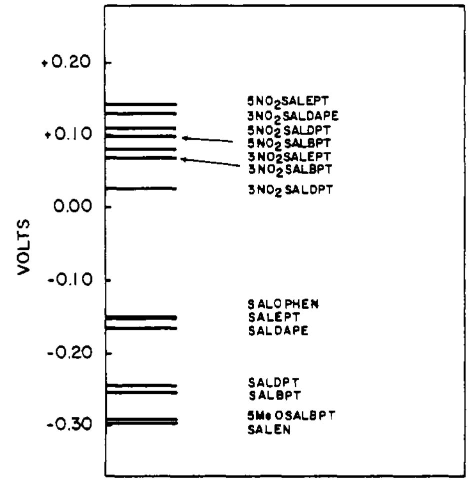
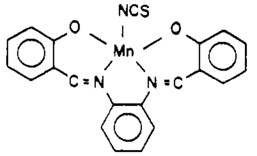


Figure 2. Manganese(III) reduction potential (E_{pc}) data from cyclic voltammetry for various ligand environments. Data not found in this paper are taken from ref 3 or 13.

sweep-rate dependence, (2) ΔE exceeding the Nernstian value of 58 mV and increasing as the sweep-rate increases, and (3) the current ratio generally being greater than 1.[12] The cyclic voltammogram (CV) for Mn(5-NO_2SALEPT)NCS (Figure 1) exhibits both the reduction and oxidation wave. No other electrochemical activity other than that shown is observed in the volatage range available in Me_2SO for Mn(SALBPT)NCS·$^1/_2H_2O$, Mn(5-CH_3OSALBPT)NCS·H_2O, Mn(SALDAPE)NCS, Mn(SALEN)Cl, and Mn(SALHTDA)NCS. For the nitro substituted complexes, the irreversible reduction of the NO_2 group is observed cathodic to −1.0 V. No evidence could be obtained for a Mn(II)/Mn(I) couple for any complex.

A substituent effect analogous to that found for Mn(ZSALDPT)NCS is also observed for these complexes; i.e., electron-withdrawing groups make the Mn(III) reduction more favorable while electron-donating groups require a more negative potential before reduction is possible (Figure 2). This trend is as expected when one considers the electrochemical reaction to be an addition of electron density to the Mn ion which can be aleviated to some degree by the electron-withdrawing power to the NO_2 group. This substituent effect is not unique to pentadentate ligands since we have recently shown[13] a similar phenomenon with tetradentate ligands, ZSALOPHEN (structure III), possessing a O_2N_2 donor set.



III

Mn(ZSALOPHEN)NCS

A second trend that was observed in the Mn(ZSALDPT)NCS complexes,[3] and observed here also, is the greater substituent effect exerted by a 5-Z group compared to the same 3-Z group; the 5-NO_2 derivatives are reduced at more positive potentials that the correspondong 3-NO_2 derivatives.

It is informative to compare manganese(III) reduction potentials for gross changes in ligand structure. Figure 2

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Table III. Cyclic Voltammetry Data for the Mn(III)/Mn(II) Reduction

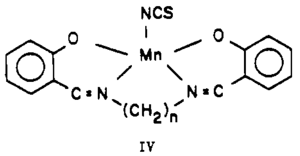
complex	ν, mV/s	E_{pc}, V	E_{pa}, V	ΔE, mV	i_{pc}, μA	i_{pc}/i_{pa}
Mn(5-NO_2SALEPT)NCS·$^1/_2H_2O$	2	+0.142	+0.216	74	2.2	1.09
	5	+0.137	+0.219	82	3.5	1.10
	10	+0.133	+0.223	90	4.8	1.13
	20	+0.127	+0.230	103	6.6	1.16
Mn(3-NO_2SALEPT)NCS·$^1/_2H_2O$	2	+0.080	+0.154	74	2.8	1.09
	5	+0.074	+0.158	84	4.3	1.14
	10	+0.068	+0.163	95	6.0	1.18
	20	+0.062	+0.170	108	8.2	1.27
Mn(SALEPT)NCS·H_2O	2	−0.152	−0.075	77	3.1	1.08
	5	−0.155	−0.072	83	4.8	1.12
	10	−0.160	−0.067	93	6.5	1.09
	20	−0.166	−0.062	104	9.0	1.10
Mn(5-NO_2SALBPT)NCS	2	+0.097	+0.193	96	2.7	1.03
	5	+0.088	+0.202	114	4.1	1.08
	10	+0.080	+0.210	130	5.6	1.09
	20	+0.068	+0.223	155	7.5	1.10
Mn(3-NO_2SALBPT)NCS·H_2O	2	+0.067	+0.163	96	2.7	1.06
	5	+0.059	+0.172	113	4.1	1.09
	10	+0.048	+0.182	134	5.6	1.09
	20	+0.035	+0.198	163	7.4	1.10
Mn(SALBPT)NCS·$^1/_2H_2O$	2	−0.255	−0.110	145	2.4	1.20
	5	−0.275	−0.088	187	3.5	1.26
	10	−0.295	−0.060	235	4.7	1.26
	20	−0.323	−0.025	298	6.3	1.29
Mn(5-CH_3OSALBPT)NCS·H_2O	2	−0.293	−0.167	126	2.5	1.07
	5	−0.302	−0.160	142	3.6	1.18
	10	−0.323	−0.135	188	4.6	1.23
	20	−0.347	−0.113	234	6.1	1.30
Mn(3-NO_2SALDAPE)NCS·H_2O	2	+0.129	+0.222	93	1.6	1.07
	5	+0.129	+0.230	169	2.4	1.09
	10	+0.111	+0.242	131	3.3	1.21
	20	+0.097	+0.257	160	4.3	1.22
Mn(SALEN)Cl	2	−0.297	−0.232	65	3.3	1.03
	5	−0.298	−0.229	69	5.2	1.04
	10	−0.302	−0.226	76	7.4	1.04
	20	−0.307	−0.223	84	10.3	1.03
Mn(SALHTDA)NCS·$^1/_2H_2O$	5	−0.140			1.3	
	10	−0.150			2.1	
	20	−0.163			3.2	

graphically represents all the measured Mn(III) reduction potentials, E_{pc}. Several points can be drawn from the relative positions of the E_{pc} values. The E_{pc} values for Mn(SALDPT)NCS and Mn(SALBPT)NCS are close to one another, and hence, both are probably five-coordinate with Me_2SO molecule occupying the sixth coordination position of Mn(III). It is well documented[14] that the seven-atom chain $((CH_2)_3NH(CH_2)_3)$ in SALDPT enables the secondary amine to coordinate with transition metals. The eight-atom chain $((CH_2)_3NH(CH_2)_4)$ in SALBPT evidently affects very little the electronic properties of Mn(III) in spite of the seven-membered chelate ring thereby produced. Furthermore, the effect of nitro substitution is comparable in both cases.

In contrast, Mn(SALEPT)NCS is reduced much easier than Mn(SALDPT)NCS or Mn(SALBPT)NCS. The E_{pc} for Mn(SALEPT)NCS compares quite favorably with the E_{pc} for Mn(SALDAPE)NCS and tetradentate Mn(SALOPHEN)NCS,[13] both of which contain N_2O_4 donor sets if one or two Me_2SO molecules complete the octahedral geometery. This observation suggests that SALEPT is acting as a tetradentate ligand with the central nitrogen not coordinated. The six-atom chain $((CH_2)_3NH(CH_2)_2)$ in SALEPT which would give rise to a five-membered chelate ring apparently does not allow the secondary amine to coordinate.

An examination of Figure 2 reveals that the approximately 100-mV difference in E_{pc} for Mn(SALEPT)NCS and Mn(SALDPT)NCS/Mn(SALBPT)NCS does not hold for their nitro-substituted derivatives. One reason for this may be that *all* nitro-substituted ligands are pentacoordinate. With electron-withdrawing groups attached to the salicylaldehyde, five-coordination has been shown[15] to be enhanced with cobalt complexes as visible spectral evidence supports a five-coordinate geometry for Co(5-NO_2SALDAPE) while Co(SALDAPE) possesses a tetrahedral geometry.[8,15]

Even though the central donor may *not* be coordinated in several of these complexes, it nevertheless must be electrochemically important. Replacement of the donor group with a methylene carbon yields a manganese(III) system, Mn(SALHTDA)NCS (structure IV), which is irreversibly reduced (Table III). The Mn(II) precursor is probably polymeric[16] while Mn(SALHTDA)NCS is monomeric. Thus the irreversibility of this species is understandable as there is no stable monomeric Mn(II) species. A surprising result is the fairly negative E_{pc} value of Mn(SaLEN)Cl (structure IV) as this ligand apparently stabilizes Mn(III) better than any of the pentadentate systems (Table III and Figure 2). The complex is a 1:1 electrolyte in Me_2SO and, if monomeric,



IV

n = 2 HSALEN
n = 7 HSALHTDA

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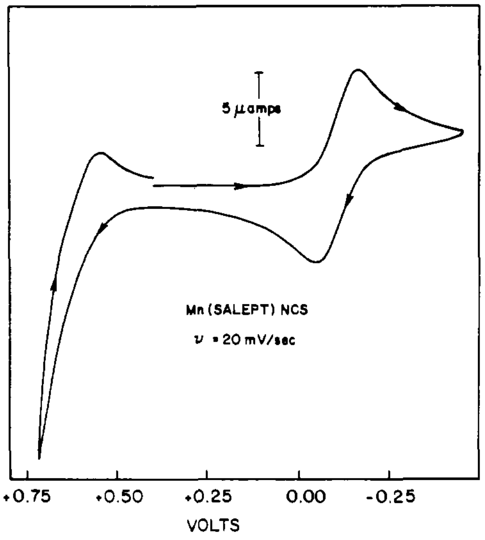

Figure 3. Cyclic voltammogram of Mn(SALEPT)NCS in dimethyl sulfoxide. Scan rate = 20 mV/s.

would have a N_2O_4 donor set. In light of its more negative reduction potential, a higher degree of coordination might be expected since it is well documented that certain HSALEN complexes of other transition metals are dimeric[17]

Cyclic voltammetry of analogous acetophenone and benzophenone DPT derivatives in place of benzaldehyde gave surprisingly ill-defined manganese(III) reductions in all cases regardless of the aromatic substituent. A rationale for this observation is not readily apparent. Copper(II) and nickel(II) complexes of Schiff base ligands derived from DPT and 2-hydroxybenzophenones have been synthesized and reported[19] to be similar to salicylaldehyde derived complexes. Extension to the manganese(III) case may not be justified. Since repeated synthesis and elemental analysis of these products continually gave slightly analytically impure samples, an impurity may account for these results.

Application of *anodic* voltages failed to give definitive evidence for oxidation of any manganese(III) complex. In the case of Mn(SALEPT)NCS, however, some cathodic current was observed at +0.54 V on the reverse scan (Figure 3). The corresponding oxidation apparently is obscured by the background current or could be due to SCN^- oxidation. With the Mn(II) precursor, Mn(SALEPT) in which no SCN^- is required, this oxidation and subsequent reduction is clearly present.[18] The oxidation may correspond to a Mn(III)/Mn(IV) process. However, in light of the fact that neither the Mn(II)[18] nor Mn(III) complexes with SALDPT or SALBPT, which have comparable or better ligand donors, exhibit such an oxidation, this suggestion appears suspect. For this discussion a better donor is assumed to stabilize the higher oxidation state. Since the SCN^- ion is common to all Mn(III) complexes and the oxidation near +0.60 V is present in Mn(SALEPT) which contains no SCN^-, oxidation and subsequent reduction of SCN^- can also be dismissed as a possibility.

The secondary amine group of EPT may provide a site for oxidation, but one must account for the fact that the amine donor apparently is unoxidized in BPT and DPT complexes and in the NO_2 derivatives of SALEPT. Dealing with the last point first, the difference between the Mn(II)/Mn(III) oxidation and the second oxidation in Mn(SALEPT),[18] Mn(SALDIEN),[18] and Mn(SAL-1,4,7,10)NCS (vide infra) appears to be ca. +0.7 V. On assumption of a comparable value for the NO_2 derivatives, any further oxidation of Mn(5-NO_2SALEPT)NCS, Mn(5-NO_2SALDPT)NCS, or Mn(5-NO_2SALBPT)NCS would be shifted out of the voltage range normally accessible in Me_2SO with SCN^- present and therefore not be observable. It is not likely, however, that the oxidation potentials of the unsubstituted BPT and DPT complexes would be shifted out of the accessible voltage range. Thus, explanation of the second oxidation in the SALEPT complex lies in suspected differences in coordination. The larger chelate rings (six- and seven-membered in DPT and BPT, respectively) allow for amine coordination, but the shorter C_2H_2 group in SALEPT may either prevent or at least diminish coordination of the amine group. Oxidation of the amine may be occurring in Mn(SALEPT)NCS, but we cannot state this with certainity. In fact, evidence below argues against this viewpoint.

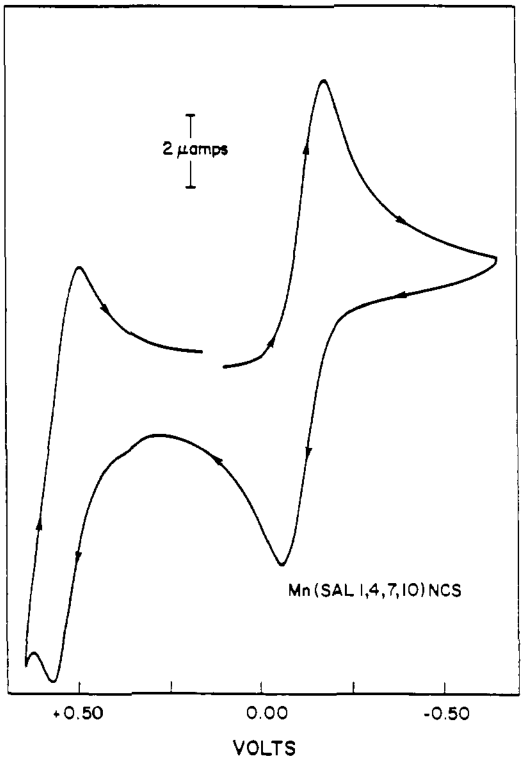

Figure 4. Cyclic voltammogram of Mn(SAL-1,4,7,10)NCS in dimethyl sulfoxide. Scan rate = 20 mV/s.

The effects on the electrochemical behavior of various chelate ring sizes with selected manganese(III) complexes of hexadentate ligands have also been investigated. The ligands are quite similar to the above pentadentate ligands being condensation products of salicylaldehyde and linear tetraamines (structure II). Synthesis and characterization of these manganese(III) complexes have been described previously.[4] A Mn(III)/Mn(II) redox couple is discerned for Mn(SAL-1,4,7,10)NCS, Mn(SAL-1,5,8,12)NCS, and Mn(SAL-1,5,9,13)NCS (Table IV) but not for Mn(5-NO_2SAL-1,4,7,10)NCS. For the NO_2 derivative, only the irreversible reduction of the NO_2 group beyond −1.0 V was observed. The reduction potentials of the three unsubstituted complexes differ by aproximately 135 mV although all contain the same potential donor set. The complex containing SAL-1,4,7,10 with all three bridging groups being C_2H_4 units is reduced at the least negative potential and near that for Mn(SALEPT)NCS. The other two hexadentate ligands SAL-1,5,8,12 and SAL-1,5,9,13 with one and no C_2H_4 units, respectively, are reduced near potentials for SALDPT and SALBPT.

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(18) W. M. Coleman, R. K. Boggess, J. W. Hughes, and L. T. Taylor, submitted for publication.

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Table IV. Electrochemical Mn(III)/Mn(II) Data for Manganese Complexes Containing Hexadentate Ligands

complex	V, mV/s	E_{pc}, V	E_{pa}, V	ΔE, mV	i_{pc}, μA	i_{pc}/i_{pa}
Mn(SAL-1,4,7,10)NCS	2	−0.140	−0.066	74	2.6	1.06
	5	−0.148	−0.065	83	4.0	1.07
	10	−0.153	−0.060	93	5.6	1.11
	20	−0.160	−0.055	105	7.6	1.13
Mn(SAL-1,5,8,12)NCS	2	−0.275	−0.192	83	3.2	1.01
	5	−0.279	−0.188	91	4.9	1.07
	10	−0.285	−0.181	104	6.7	1.08
	20	−0.296	−0.170	126	9.0	1.08
Mn(SAL-1,5,9,13)NCS·$^1/_2H_2O$	2	−0.228	−0.099	129	2.6	1.03
	5	−0.245	−0.090	155	3.8	1.02
	10	−0.253	−0.090	163	5.3	0.99
	20	−0.268	−0.087	181	7.2	0.98

Mn(SAL-1,4,7,10)NCS and Mn(SAL-1,5,8,12)NCS exhibit a quasi-reversible oxidation similar to that of Mn(SALEPT)NCS discussed above. The oxidation and subsequent reduction is well defined in Mn(SAL-1,4,7,10)NCS (Figure 4) in contrast to the other complexes. The origin of this oxidation remains a mystery but is clearly related to those ligands with one or more bridging C_2H_4 groups. Crystal structures of Fe(SAL-1,4,7,10)X (X = Cl·$2H_2O$ and NO_3·H_2O)[20] show unequivocally that this ligand can accommodate the short C_2H_4 bridging groups and coordinate as a hexadentate ligand with little steric strain. If the Mn(III) complex also contains a hexadentate ligand (as is believed to be the case[4]), then oxidation of a noncoordinated amine is not the source of this oxidation.

In conclusion, the stabilization of manganese(III) has been demonstrated to be determined only in part by the ligand donor atom set. With the same donor set dramatic changes in redox potential and reversibility can be created by different aromatic ring substituents, different chelate ring sizes and different α-carbon substituents. An oxidation of unknown origin occurs in the Mn(III) complexes containing ligands with a C_2H_4 bridging group. The influence of analogous ligand modifications on the stability of manganese(II) will be dealt with in a forthcoming manuscript.

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Registry No. Mn(5-NO_2SALEPT)NCS, 76430-54-1; Mn(3-NO_2SALEPT)NCS, 76430-55-2; Mn(SALEPT)NCS, 76430-56-3; Mn(5-NO_2SALBPT)NCS, 76430-57-4; Mn(3-NO_2SALBPT)NCS, 76430-58-5; Mn(SALBPT)NCS, 76430-59-6; Mn(5-CH_3OSALBPT)NCS, 76430-60-9; Mn(3-NO_2SALDAPE)NCS, 76430-61-0; Mn(SALDAPE)NCS, 70754-27-7; Mn(SALHTDA)NCS, 76430-62-1; Mn(SALEN)Cl, 53177-12-1; Mn(SAL-1,4,7,10)NCS, 76430-63-2; Mn(SAL-1,5,8,12)NCS, 76430-64-3; Mn(SAL-1,5,9,13)NCS, 76430-65-4; SAL, 90-02-8; 5-NO_2SAL, 97-51-8; 3-NO_2SAL, 5274-70-4; BPT, 124-20-9; DAPE, 2157-24-6; EPT, 13531-52-7.

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Kinetics and Mechanism of the Regiospecific Alkylation of Cobaloxime–Tetrazole Complexes

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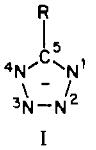
A series of complexes of the type (*n*-Bu_3P)Co$(DH)_2$(5-R-tetrazolate) (DH is the monoanion of dimethylglyoxime; R = CF_3, CH_3, C_6H_5, $C_6H_5CH_2$, $(CH_3)_2N$, 4-FC_5H_4, and 3-FC_6H_4) have been treated with a variety of alkylating agents. NMR spectral comparison with known compounds revealed that in each case regiospecific alkylation of the coordinated tetrazolate produced exclusively 1,5-disubstituted tetrazoles. None of the isomeric 2,5-disubstituted tetrazoles were formed, in marked contrast to all previous alkylations of tetrazoles where mixtures of the two isomers are always formed. The results of ^1H NMR monitored kinetic experiments under pseudo-first-order conditions indicated that the alkylations proceed by two consecutive steps. Long-lived intermediates were spectroscopically observed in the alkylations of the 5-methyl- and 5-benzyltetrazolate complexes. The rate constants and activation parameters are consistent with an overall second-order nucleophilic attack of the alkyl halide on the coordinated tetrazolate to form an intimately associated charged intermediate. Formation of the intermediate is followed by a dissociative interchange of halide and 1,5-disubstituted tetrazole producing (*n*-Bu_3P)Co$(DH)_2$X and liberating free 1,5-disubstituted tetrazole. Alkylation of the 5-(*N*,*N*-dimethylamino)tetrazolate complex involves initial attack at the exocyclic amino nitrogen followed by an unusual inner-sphere migration of the alkyl group to an N-1 ring site of the coordinated tetrazolate The relationship of these studies to other investigations of the alkylations of tetrazoles is discussed.

Introduction

Recently[1] we described the preparation and characterization (spectroscopic and crystallographic) of a series of complexes of the type Co$(DH)_2$(5-R-tetrazolate). One purpose in preparing these complexes was to determine whether the steric environment imposed on the tetrazolate ligand by the equitorial oxime ligands was sufficient to induce regiospecific coordination of the ambidentate, anionic 5-R-tetrazolate rings (I) via the less hindered N_2 nitrogen. NMR and X-ray crystallographic data showed that this objective was fully realized. Each of the complexes contained exclusively N_2 coordinated tetrazolate regardless of the electronic properties of the 5-



I

tetrazolate ring numbering scheme

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