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Preparation and Electrochemical Studies of Tetradentate Manganese(III) Schiff Base Complexes

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Manganese(III) complexes employing a variety of monovalent anions and the dianionic Schiff base tetradentate ligand derived from ortho-*phenylenediamine and various substituted salicylaldehydes have been prepared and characterized. Cyclic voltammetry experiments on these high spin manganese materials reveal a quasireversible Mn(III)/Mn(II) redox and a pronounced salicylaldehyde substituent effect on cathodic peak potential. The data can be rationalized in terms of an electronic effect except in the 3-methoxy case where a more distorted geometry about manganese(III) can be anticipated.*

Introduction

The extent and nature of dioxygen reactivity with manganese(II) chelates are dependent on the ligand environment [1] about the manganese center which in part determines the latter's redox properties. This effect has been dramatically shown [2, 3] with several of the complexes illustrated in Structure IA and IB. Materials with electron-withdrawing substituents were shown to differ significantly in their dioxygen reactivity pattern when compared with complexes possessing electron donating groups. With nitro aromatic substituents ligand oxidation was sufficiently inhibited so that several postulated μ-peroxo manganese(III) products were isolated and characterized. Reaction [4] of these same complexes with nitric oxide showed a more marked substituent effect but in this case manganese(I) adducts were produced. As expected electron withdrawing groups on the aromatic portion of the ligand yielded the most stable manganese nitrosyls.

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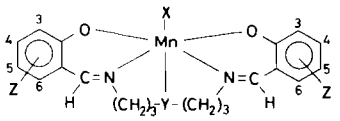


Ia. Mn(ZSALDPT)X
Y = NH, NCH_3, NC_3H_7, NC_6H_5
Z = 5-NO_2, 3-NO_2, 5-Cl, 5-Br, H, 3-MeO, 5-MeO, 5-Me
X = NCS^-, I^-, NO_2^-, N_3^-

Ib. Mn(ZSALDAPE)X
Y = O
Z = 5-NO_2, 3-NO_2-H
X = NCS

STRUCTURE I

To determine if a correlation exists between the chemical reactivity toward dioxygen and electrochemical properties, the redox characteristics of several Mn(III) complexes of SALDPT were studied [5]. It was observed that the Mn(III) complexes with electron-withdrawing groups on the aromatic ring exhibited a lower reduction potential relative to those complexes with electron-donating groups. Further, if the central ligand atom (Y) or the substituent on the central N were changed, the reduction potential of the Mn(III) was also affected.

We have now extended our studies to a rigid, planar tetradentate ligand system (Structure II) and we report the synthesis and electrochemical properties of these complexes herein.

Experimental

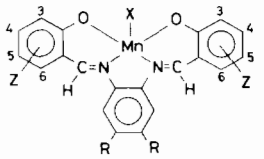
Synthesis

The complexes were prepared under N_2 initially by (1) pre-forming in ethanol the Schiff base ligand

TABLE I. Analytical Data, Magnetic Moments, and Molar Conductivity Values for Mn(ZSALOPHEN)X Complexes.

Complex	Calculated			Found			μ(B.M.)	Λ_m $\left(\frac{cm^2}{ohm\ mol}\right)$
	%C	%H	%N	%C	%H	%N		
Mn(SALOPHEN)NCS	59.01	3.30	9.83	58.83	3.32	9.97	4.88	35
Mn(SALOPHEN)I·H_2O	47.93	3.07	5.33	47.89	3.69	5.19	4.78	35
Mn(SALOPHEN)N_3	58.41	3.43	17.03	58.23	3.70	15.93	4.62	32
Mn(SALOPHEN)NO_2·$\frac{1}{2}H_2O$	56.62	3.56	9.90	57.01	3.57	9.40	4.78	36
Mn(3-MeOSALOPHEN)NCS·H_2O	54.67	3.99	8.31	54.53	4.14	8.09	4.82	34
Mn(3-MeOSALOPHEN)I	47.51	3.26	5.04	47.51	3.39	4.78	4.89	33
Mn(3-MeOSALOPHEN)N_3·$\frac{1}{4}H_2O$	55.53	3.89	14.72	55.53	4.03	12.29	4.87	29
Mn(5-ClSALOPHEN)NCS·H_2O	49.04	2.75	8.17	48.78	2.94	7.59	4.75	36
Mn(SAL-4,5-DiMeOPHEN)NCS	60.80	3.99	9.25	60.69	4.24	8.96	4.88	38
Mn(5-MeOSALOPHEN)NCS	56.67	3.73	8.62	56.61	3.80	8.58	4.87	37
Mn(4,6-DiMeOSALOPHEN)NCS	54.64	4.41	7.65	54.88	4.19	7.54	4.86	35

[a]In DMSO, C = 10^{-3} *M*.



X = NCS^-, I^-, NO_2^-, N_3^-
Z = 5-Cl, 3-MeO, H, 5-MeO, 4,6-DiMeo
R = H, CH_3

STRUCTURE II

from the appropriate salicylaldehyde (ZSAL) and *ortho*-phenylenediamine (OPHEN), (2) addition of a stoichiometric quantity of $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ in ethanol followed by (3) an excess of the salt containing the desired anion. After refluxing the reaction mixture for several minutes, the N_2 atmosphere was replaced by bubbling O_2 into the solution. The deep red precipitate which formed almost immediately was filtered, recrystallized from methanol, and dried at 90 °C *in vacuo*. More complete details of analogous syntheses can be found in the literature [6].

Electrochemistry

All measurements were done at 10^{-3} *M* in dimethylsulfoxide (DMSO) using tetraethylammonium perchlorate as the supporting electrolyte. Measurements were made with a PAR 174A polarographic analyzer equipped with a Houston Model 9002A X-Y recorder and utilizing a three-electrode geometry. The working electrode was a Beckman platinum button and the auxillary electrode was a coil of Pt wire. A saturated calomel electrode which was separated from the DMSO solution by a NaCl–agar salt bridge with a medium glass frit served as the reference electrode. Other experimental conditions have been previously reported [5].

Measurements

Visible spectra were recorded in DMSO solution using a Hitachi Model 100-60 spectrophotometer. Infrared spectra were recorded as Nujol mulls using a Beckman Model 20A-X spectrophotometer. Magnetic susceptibility data were obtained at room temperature by the Faraday method using Hg(Co(SCN)$_4$) and Ni(en)$_3$(S_2O_3) as calibrants. Diamagnetic corrections were made employing Pascal's constants. Conductivity data in DMSO were obtained using an Industrial Instruments, Inc. Model RC-16B2 conductivity bridge.

Results and Discussion

Manganese(III) complexes employing a monovalent anion and a Schiff base tetradentate ligand (Structure II) derived from various substituted salicylaldehydes (ZSAL) and *ortho*-phenylenediamine (OPHEN) have been prepared and characterized. Physical data are listed in Table I. Magnetic moment measurements (4.9 B.M.) confirm the presence of a Mn(III) ion. In contrast to the ZSALDPT complexes, neither Mn(5-NO_2SALOPHEN)X nor Mn(3-NO_2SALOPHEN)X could be obtained using O_2 to oxidize the Mn(II) precursors. While this result was somewhat surprising, it was nevertheless consistent with our observation that the rate and extent of oxidation of Mn(ZSALDPT) complexes are retarded by electron-withdrawing groups. It is interesting to note, moreover, that a halogen substituent (5-Br) on SALOPHEN also renders iron(II) oxygen insensi-

TABLE II. Electronic Spectra of Mn(ZSALOPHEN)X.

Complex	$\lambda(\epsilon)$[a]
H_2SALOPHEN	450(sh), 360(sh), 333(18,600)
Mn(SALOPHEN)NCS	585(sh), 530(sh), 424(11,000), 340(31,000)
Mn(SALOPHEN)I·H_2O	575(sh), 535(sh), 425(9,900), –
Mn(SALOPHEN)NO_2·½H_2O	585(sh), 540(sh), 422(10,600), –
Mn(SALOPHEN)N_3	575(sh), 535(sh), 422(10,400), –
Mn(5-ClSALOPHEN)NCS·H_2O	595(sh), 550(sh), 425(10,200), –
Mn(SAL-4,5-DiMeOPHEN)NCS	595(sh), 547(sh), 424(12,200), –
Mn(5-MeOSALOPHEN)NCS	650(sh), 455(sh), 383(sh), 350(sh), (24,800), 335(36,400), 305(37,000)
Mn(4,6-DiMeOSALOPHEN)NCS	585(sh), 570(sh), 415(sh), 385(33,000)
Mn(3-MeOSALOPHEN)NCS·H_2O	595(sh), 445(sh), 362(29,300), 312(26,000)
Mn(3-MeOSALOPHEN)I	600(sh), 440(sh) – –
Mn(MeOSALOPHEN)N_3·¼H_2O	595(sh), 445(sh) – –

[a]In DMSO at 10^{-3} to 10^{-5} *M*.

tive [7] whereas the unsubstituted analog readily reacts with O_2. This was not the case with halogen substituents in our study as Mn(5-ClSALOPHEN)NCS was easily prepared.

The primary counter-ion in this study has been thiocyanate ion although several azide, iodide and nitrite complexes are reported. It should be noted here that the synthesis and magnetic properties of a limited number of Mn(ZSALOPHEN)X complexes wherein X = acetate and hydroxide have previously been briefly communicated [8]. The temperature dependence of the magnetic moment of these complexes was attributed to a weak antiferromagnetic interaction. No further characterization of these materials was presented.

The structure of the complexes in the solid state is presumably 5-coordinate with ZSALOPHEN functioning as a tetradentate ligand and the fifth coordination site occupied by an anion (NCS^-, N_3^-, NO_2^-, or I^-). The C–N stretch of the NCS^- group occurs between 2050 and 2070 cm^{-1} in the complexes which is consistent with N-coordination [9]. The C–S band near 800 cm^{-1} cannot be located due to strong ligand bands in this region. The coordination mode of the NO_2^- anion cannot be deduced with certainty because of strong ligand bands in the 1400 cm^{-1} region. However, there is a noticeable absence of any band near 1065 cm^{-1} which is usually present for the nitrito (–ONO) isomer [10]. Thus, it is likely that the NO_2^- is coordinated as the nitro (–NO_2) anion. Coordinated azide absorptions in the two complexes prepared here occur at 2030 and 2020 cm^{-1}. Ligand absorptions (such as C=N str.) are in good agreement with known literature values for similar type complexes [12].

The electronic spectra of the complexes dissolved in DMSO were recorded between 800 and 300 nm

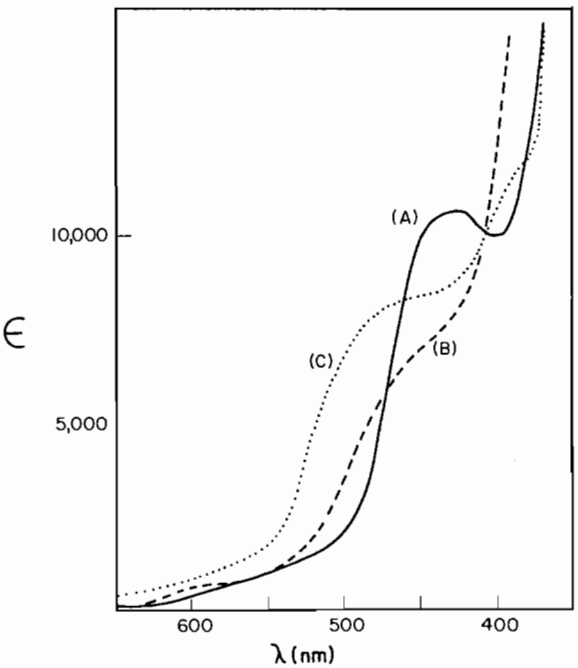


Fig. 1. Visible spectra of (A) Mn(SALOPHEN)NCS, (B) Mn(3-MeOSALOPHEN)NCS, (C) Mn(5-MeOSALOPHEN)-NCS in DMSO.

(Table II, Fig. 1). The parent ligand (SALOPHEN) spectrum exhibits two shoulders above 350 nm and an intense band at 333 nm ($\pi \rightarrow \pi^*$, azomethine). Absorption maxima occurring in the visible region of the complexes appear as shoulders on a main peak(s) (<500 nm) which maximizes in the ultraviolet. The peak no doubt is a combination of metal-to-ligand charge transfer and intraligand transitions. As might be expected the spectral features of these complexes

TABLE III. Cyclic Voltammetry Data for the Mn(III) → Mn(II) Reduction. Aromatic Substituent Effect.

Complex	Concentration (m*M*)	ν(mV/sec)	E_{Pc} (V)	E_{Pa} (V)	ΔE (mV)	i_{Pc}(μamps)	i_{Pc}/i_{Pa}
Mn(5-ClSALOPHEN)NCS·H_2O	1.0	1	−0.042	+0.027	69	2.3	0.98
		2	−0.043	+0.027	70	3.2	1.04
		5	−0.047	+0.029	76	5.0	1.04
		10	−0.052	+0.035	87	6.9	1.03
Mn(3-MeOSALOPHEN)NCS·H_2O	1.0	1	−0.119	−0.049	70	2.2	0.97
		2	−0.116	−0.049	67	3.2	1.05
		5	−0.118	−0.047	71	4.9	1.02
		10	−0.122	−0.044	78	6.8	1.04
Mn(SALOPHEN)NCS	1.0	1	−0.151	−0.086	65	2.3	1.02
		2	−0.153	−0.086	67	3.3	1.02
		5	−0.155	−0.084	71	5.1	1.02
		10	−0.158	−0.082	76	7.1	1.02
Mn(SAL-4,5-DiMeOPHEN)NCS	1.0	1	−0.181	−0.106	75	2.3	0.99
		2	−0.185	−0.107	78	3.2	1.03
		5	−0.192	−0.103	89	4.9	1.07
		10	−0.204	−0.093	11	6.6	1.05
Mn(5-MeOSALOPHEN)NCS	1.0	1	−0.200	−0.130	70	2.2	1.05
		2	−0.200	−0.130	70	3.0	1.07
		5	−0.203	−0.122	76	4.7	1.09
		10	−0.210	−0.122	88	6.5	1.06
Mn(4,6-DiMeOSALOPHEN)NCS	1.0	1	−0.240	−0.167	73	2.2	1.02
		2	−0.240	−0.162	78	2.9	1.05
		5	−0.242	−0.157	85	4.3	1.05
		10	−0.248	−0.150	98	5.9	1.05

are very similar to those previously reported for closely related Mn(SALEN)X [13], Mn(acen)X [14] and other manganese(III) chelates [15]. It, therefore, seems plausible to propose that the low energy shoulder(s) between 500 and 600 nm is (are) a d–d transition. In octahedral notation this would correspond to $^5E_g \rightarrow {}^5T_{2g}$ or its components in one or another lower symmetry group. The appearance of only one shoulder in this region for methoxy derivatives whereas two shoulders are observed for the other derivatives is probably due to greater absorption in the UV for the former complexes. The position of the lowest energy band does not change within experimental error regardless of the anion or aromatic substituent. This is not surprising concerning the anion since all complexes behave as 1:1 electrolytes in DMSO [16] (Table I). The insensitivity of the d–d transition to SAL substituent, however, was not anticipated since the cyclic voltammetry data showed a marked substituent dependence (*vide infra*). Visible spectra in the solid state as Nujol mulls were also measured above 400 nm. The spectra possessed the same features as solution spectra except each shoulder was considerably less pronounced and shifted slightly to longer wavelength.

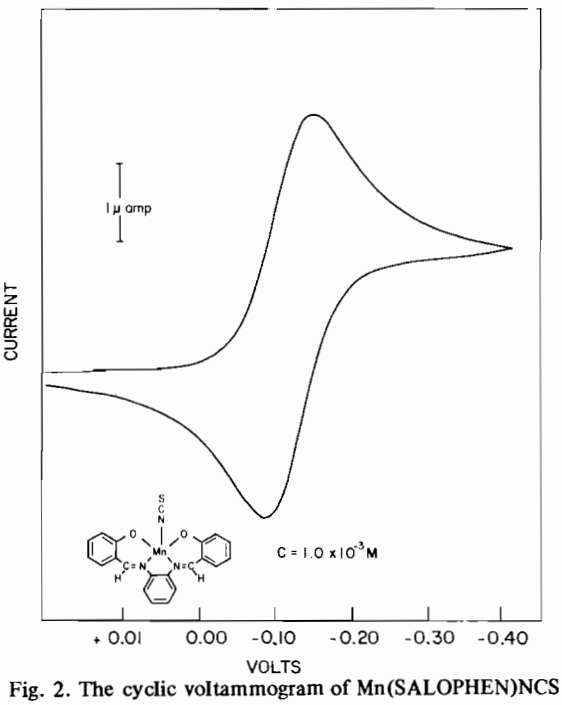


Fig. 2. The cyclic voltammogram of Mn(SALOPHEN)NCS in DMSO.

TABLE IV. Cyclic Voltammetry Data for the Mn(III) → Mn(II) Reduction. Anion Effect.

Complex	Concentration (m*M*)	(mV/sec)	E_{Pc}	E_{Pa}	ΔE (mV)	i_{Pc}(μamps)	i_{Pc}/i_{Pa}
Mn(SALOPHEN)NCS	1.0	1	−0.151	−0.086	65	2.3	1.02
		2	−0.153	−0.086	67	3.3	1.02
		5	−0.155	−0.084	71	5.1	1.02
		10	−0.158	−0.082	76	7.1	1.02
Mn(SALOPHEN)I·H_2O	1.0	1	−0.151	−0.082	69	1.9	1.03
		2	−0.153	−0.082	71	2.9	1.03
		5	−0.155	−0.078	77	4.6	1.05
		10	−0.158	−0.073	85	6.3	1.04
Mn(SALOPHEN)NO_2·½H_2O	1.0	1	−0.158	−0.087	71	2.3	0.92
		2	−0.160	−0.085	75	3.2	1.02
		5	−0.162	−0.082	80	5.0	1.07
		10	−0.169	−0.076	93	6.8	1.05
Mn(SALOPHEN)N_3	1.0	1	−0.160	−0.078	82	2.3	1.04
		2	−0.160	−0.078	82	3.1	1.03
		5	−0.167	−0.072	95	4.7	1.06
		10	−0.172	−0.063	09	6.4	1.06
Mn(3-MeOSALOPHEN)NCS·H_2O	1.0	1	−0.115	−0.049	70	2.2	0.97
		2	−0.116	−0.049	67	3.2	1.05
		5	−0.118	−0.047	71	4.9	1.02
		10	−0.122	−0.044	78	6.8	1.04
Mn(3-MeOSALOPHEN)I	1.0	1	−0.115	−0.051	64	2.3	1.04
		2	−0.116	−0.050	65	3.2	1.02
		5	−0.118	−0.050	68	5.0	1.02
		10	−0.122	−0.048	74	7.1	1.01
Mn(3-MeOSALOPHEN)N_3·¼H_2O	1.0	1	−0.130	−0.062	68	2.3	1.01
		2	−0.130	−0.062	68	3.2	1.01
		5	−0.133	−0.059	74	4.9	1.02
		10	−0.137	−0.056	81	6.8	1.02

The cyclic voltammetry data obtained for the Mn(III) → Mn(II) reduction of the complexes in DMSO are presented in Tables III and IV. No other reductions within the solvent range of −1.8 V were observed except with Mn(5-CLSALOPHEN)NCS (−1,58 V) and Mn(5-MeOSALOPHEN)NCS (−1.68 V). These reductions are irreversible, probably involve the reduction of the ligand, and were not investigated further. No oxidations were observed in any of the complexes except those containing I^- for which the irreversible oxidation of I^- was observed at +0.12 V.

Several main points regarding the data in Tables III and IV that require discussion are (1) the characteristics of the reduction reaction in terms of reversibility, (2) the extent of the reduction reaction, (3) the effect of various substituents attached to the ligand, and (4) the dependence of the reduction on the counterion.

The cyclic voltammogram of Mn(SALOPHEN)NCS is illustrated in Fig. 2 as a typical example of the reduction and subsequent oxidation of the complexes. No reductions near the potentials reported in Tables III and IV were observed for the free ligand H_2SALOPHEN and thus the reductions and subsequent oxidations are assigned to the Mn(III) ⇄ Mn(II) process. This assignment is reasonably straightforward although it is likely that the electron enters a molecular orbit which is predominantly metal in character but with some ligand contribution.

A completely reversible, Nernstian one-electron transfer will have an E_p value independent of scan rate, a ΔE value of 58 mV, and a ratio of 1.00 for cathodic to anodic peak currents [17, 18]. For all of the complexes reported in Table III, the E_p values shift with an increase in scan rate, the ΔE values approach 58 mV only at slow scan rates, and the current ratios generally give values slightly in excess of 1.00. Plots of i_p *versus* the square root of scan rate (Fig. 3) and i_p *versus* concentration at a fixed scan rate are linear. These data indicate that

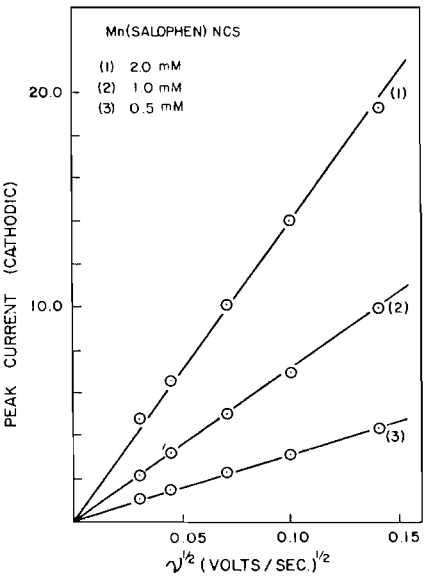


Fig. 3. Cathodic peak current *versus* the square root of the scan rate for Mn(SALOPHEN)NCS.

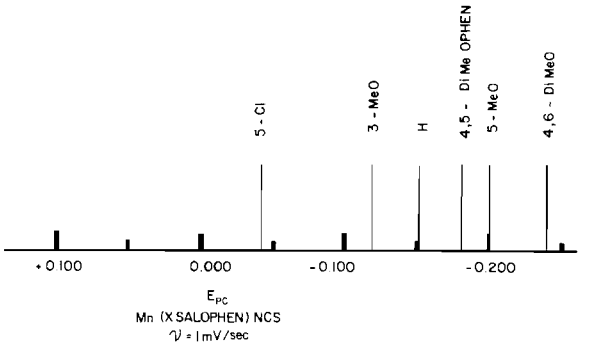


Fig. 4. The relative cathodic peak positions for the reduction of the Mn(ZSALOPHEN)NCS complexes in DMSO.

the electron transfer reaction is of the quasireversible type.

The electrochemical properties of the complexes generally show the substituent effect as observed for Mn(ZSALDPT)X complexes [5] (Fig. 4). The complex containing an electron-withdrawing substituent, Mn(5-ClSALOPHEN)NCS, is reduced at a potential anodic to that of Mn(SALOPHEN)NCS while the complexes containing electron-donating methyl or methoxy groups (with the exception of 3-MeO) are reduced at potentials cathodic to that of Mn(SALOPHEN)NCS. These results are also consistent with the fact that nitro substituted Mn(SALOPHEN) complexes are not oxidized by molecular oxygen. Moreover, the ease of reduction of the complexes is in the order Mn(SAL-4,5-DiMeOPHEN)NCS > Mn(5-MeOSALOPHEN)NCS > Mn(4,6-DiMeOSALOPHEN)NCS. In other words, two methyl groups on the OPHEN portion of the ligand are less effective than two methoxy groups on the two SAL portions of the ligand in donating electron density. Likewise Mn(5-MeOSALOPHEN)NCS is reduced more easily than Mn(4,6-DiMeOSALOPHEN)NCS. It is also interesting to note that the spectrum of Mn(SAL-4,5-DiMeOPHEN)NCS resembled those of the Mn(SALOPHEN)NCS complex rather than the complexes containing a MeO group on the SAL portion of the ligand.

The reduction potential of Mn(3-MeOSALOPHEN)NCS is completely unexpected as one would predict a value between the reduction potentials for Mn(SALOPHEN)NCS (–0.153 V) and Mn(5-MeOSALOPHEN)NCS (–0.200 V). As is seen from Fig. 4, the reduction potential of Mn(3-MeOSALOPHEN)NCS is anodic, not cathodic, to that of Mn(SALOPHEN)NCS. Inspection of molecular models shows that a nearly planar arrangement of the ligand is possible for the SALOPHEN complexes. If two bulky substituents, such as methoxy groups, replace the hydrogens in the 3 position, some crowding between the two methoxy groups occurs with a resulting tilt of the two SAL aromatic rings out of the planar arrangement. This causes a less favorable orientation of the coordinating hydroxy oxygen atoms and thus may make 3-MeOSALOPHEN a poorer donor overall than SALOPHEN even though the 3-MeO group is electron donating. No steric interference of methoxy groups would be possible when the 5 position is substituted. Steric problems were not encountered in the Mn(ZSALDPT)NCS complexes due to the more flexible nature of the ligand.

For the three complexes where direct comparisons are possible, Mn(ZSALDPT)NCS complexes are reduced 100 ± 10 mV cathodic to Mn(ZSALOPHEN)NCS complexes (Table V). This is probably the result of (1) better delocalization of the added electron density through the π system of the ZSALOPHEN ligand and (2) the absence in ZSALOPHEN of a fifth strongly coordinating atom as in ZSALDPT. In DMSO solution, the immediate coordination sphere of the Mn(III) in the ZSALOPHEN complexes is probably 2 N and 4 O atoms (*i.e.* 2 N and 2 O atoms from ZSALOPHEN and 2 O from DMSO) while that in the ZSALDPT complexes is 3 N and 3 O atoms (*i.e.* 3 N and 2 O atoms from ZSALDPT and one O atom from DMSO). Since nitrogen atoms are typically better donors than oxygen atoms, one would expect a higher electron density and thus more cathodic reduction potentials for the Mn(ZSALDPT)NCS complexes. It is also interesting to note that the reduction potentials of Mn(SALOPHEN)NCS and Mn(SALDAPE)NCS, both of which contain N_2O_4 donor sets, are similar (–0.153 V and –0.167 V, respectively).

TABLE V. Comparison of the Reduction Potentials of Mn(ZSALOPHEN)NCS and Mn(ZSALDPT)NCS (ν = 2mV/sec, C = 1.0 × 10^{-3} *M*).

Complex	E_{Pc}	Complex	E_{Pc}
Mn(5-ClSALOPHEN)NCS	−0.043	Mn(5-ClSALDPT)NCS	−0.150
Mn(SALOPHEN)NCS	−0.153	Mn(SALDPT)NCS	−0.245
Mn(5-MeOSALOPHEN)NCS	−0.200	Mn(5-MeOSALDPT)NCS	−0.290

Finally, as was the case for the Mn(ZSALDPT)X complexes there is a slight dependence of the reduction potentials on the anion (Table IV) for both the Mn(SALOPHEN)X and Mn(3-MeOSALOPHEN)X where X = NCS^-, I^-, NO_2^-, and N_3^-. The complexes are basically 1:1 electrolytes in DMSO (Table I) and one would expect little or no anion dependence. The effect is slight (~0.015 V) and generally follows the order previously found [5] and also the order found for a series of Mn(III)–porphyrin complexes [19].

Acknowledgments

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