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Electrochemical Studies on a Series of Manganese(III) Complexes Containing Symmetrical Pentadentate Ligands

W. M. Coleman,[†1a] R. R. Goehring,[1a] L. T. Taylor,*[1a] J. G. Mason,[1a] and R. K. Boggess[1b]

Contribution from the Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, and the Department of Chemistry, Radford University, Radford, Virginia 24142. Received August 28, 1978

Abstract: The redox properties of a series of manganese(III) complexes incorporating dianionic pentadentate Schiff-base ligands have been examined using cyclic voltammetry. Substituents on the aromatic portion of the ligand and changes on the central donor atom were shown to cause changes in the reduction potentials of the Mn(III) ion. Electron-withdrawing substituents on the aromatic portion of the ligand resulted in a lower reduction potential relative to complexes possessing ligands with electron-donating groups. Changes in the reduction potential were also dependent upon the type of central donor atom and its substituent. Correlation of electrochemical data on these complexes with previously observed reactivity patterns of several of the same complexes with dioxygen and nitric oxide is described.

Introduction

The role that manganese plays in the photosynthetic liberation of dioxygen from water and the electron-transfer reactions of mitochondrial superoxide dismutase are undoubtedly related to the ability of the manganese ion to function as a redox catalyst.[2] The capacity of the metal ion to change between oxidation states can be related in part to the ligand field produced about the metal ion.[3] In this regard the oxidation state accessibility of manganese has been explored[4,5] using a variety of macrocyclic ligands. A dinegatively charged unsaturated macrocyclic ligand was observed to stabilize Mn(III) relative to a ligand that is uncharged and saturated. Ring size was also shown in this study to be important in stabilizing certain manganese oxidation states.

The extent and nature of dioxygen reactivity with manganese(II) chelates is also dependent in part on the latter's redox properties. Two reports have recently appeared which deal with the electronic effect of various ligand aromatic substituents on the reactivity of certain manganese(II) complexes toward dioxygen and nitric oxide.[6,7] Complexes with electron-withdrawing substituents were shown to differ significantly in their dioxygen reactivity pattern when compared with complexes possessing electron-donating substituents. In two cases (3-NO_2, 5-NO_2) ligand oxidation was inhibited sufficiently so that several manganese(III) products were obtained depending

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[†] University of California, Berkeley, Naval Biosciences Laboratory, Naval Supply Center, Oakland, Calif. 94625.

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Table I. Cyclic Voltammetry Data for the Mn(III) → Mn(II) Reduction: Aromatic Substitution Effect

complex	concn, M	ν, mV/s	E_{p_c}, V	E_{p_a}, V	ΔE, mV	i_{p_c}, μA	i_{p_c}/i_{p_a}
Mn(5-NO_2SALDPT)NCS	1.0×10^{-3}	2	+0.110	+0.188	78	2.7	1.00
		5	+0.107	+0.192	85	4.2	1.00
		10	+0.104	+0.196	92	5.8	1.02
		20	+0.098	+0.203	105	8.0	1.01
	5.0×10^{-4}	2	+0.107	+0.182	75	1.6	1.01
		5	+0.105	+0.187	82	2.5	1.00
		10	+0.101	+0.190	89	3.3	1.04
		20	+0.097	+0.195	98	4.5	0.99
Mn(3-NO_2SALDPT)NCS	1.0×10^{-3}	2	+0.025	+0.083	58	2.9	1.05
		5	+0.021	+0.083	62	4.3	1.03
		10	+0.018	+0.088	70	6.7	1.03
		20	+0.016	+0.087	71	9.4	1.02
	5.0×10^{-4}	2	+0.021	+0.090	69	1.6	1.08
		5	+0.020	+0.093	73	2.4	1.01
		10	+0.018	+0.095	77	3.3	1.01
		20	+0.015	+0.098	83	4.7	1.03
Mn(5-ClSALDPT)NCS	1.0×10^{-3}	2	−0.150	−0.079	71	2.8	1.06
		5	−0.152	−0.076	76	4.4	1.04
		10	−0.155	−0.074	81	6.1	1.03
		20	−0.160	−0.068	92	8.2	1.01
	5.0×10^{-4}	2	−0.153	−0.073	80	1.4	1.04
		5	−0.156	−0.068	88	2.2	1.06
		10	−0.163	−0.065	98	3.0	1.10
		20	−0.170	−0.057	113	4.1	1.07
Mn(SALDPT)NCS	1.0×10^{-3}	2	−0.245	−0.172	73	3.2	1.03
		5	−0.247	−0.168	79	5.1	1.04
		10	−0.252	−0.165	87	7.0	1.04
		20	−0.257	−0.158	99	9.6	1.05
	5.0×10^{-4}	2	−0.240	−0.168	72	1.7	1.07
		5	−0.241	−0.165	76	2.5	1.06
		10	−0.245	−0.161	84	3.5	1.06
		20	−0.247	−0.156	91	4.8	1.06
Mn(5-CH_3SALDPT)NCS	5.0×10^{-4}	2	−0.272	−0.204	68	1.4	1.04
		5	−0.274	−0.202	72	2.3	1.05
		10	−0.276	−0.200	76	3.2	1.06
		20	−0.280	−0.196	84	4.5	1.07
Mn(3-CH_3OSALDPT)NCS	1.0×10^{-3}	2	−0.279	−0.193	86	2.5	1.03
		5	−0.287	−0.187	100	3.7	1.03
		10	−0.295	−0.177	118	5.0	1.06
		20	−0.307	−0.165	142	6.7	1.09
Mn(5-CH_3OSALDPT)NCS	1.0×10^{-3}	2	−0.290	−0.213	77	2.8	1.05
		5	−0.294	−0.208	86	4.4	1.11
		10	−0.298	−0.203	95	5.8	1.06
		20	−0.307	−0.197	110	8.0	1.12
Mn(NAPDPT)NCS	1.0×10^{-3}	2	−0.303	−0.236	67	2.8	1.07
		5	−0.303	−0.233	70	4.5	1.06
		10	−0.304	−0.232	72	6.4	1.06
		20	−0.307	−0.230	77	8.8	1.06

upon wet or dry reaction conditions.[8] Reaction with nitric oxide resulted in reduction of manganese. The resulting reversible adducts were found to be most stable with electron-withdrawing substituents attached to the aromatic portion of the pentadentate ligand. If electron effects are truly accounting for these reactivity patterns, then this phenomenon should manifest itself in electrochemical studies. In this regard, we wish to report herein an electrochemical investigation of a series of manganese(III) complexes incorporating linear pentadentate ligands which differ in aromatic substituent and in the central donor atom.

Experimental Section

Materials. Dimethyl sulfoxide (Me_2SO) (Matheson Coleman and Bell and Fisher Scientific Co.) was reagent grade and used as provided. All solutions were prepared in a nitrogen-filled glovebag as we experienced difficulties with Me_2SO exposed to the laboratory atmosphere. The supporting electrolyte tetraethylammonium perchlorate (TEAP) (Eastman Organic Chemicals) was recrystallized three times from water and dried at 60 °C in vacuo prior to use. The potential range of Me_2SO corresponded closely to that previously cited.[9] Solutions were deoxygenated by means of a stream of dry nitrogen using a fritted glass bubbler. A nitrogen blanket was maintained above the solutions during the electrochemical measurements. The synthesis of most of the complexes has been reported previously.[10] New complexes were prepared in an analogous fashion. All gave satisfactory elemental analysis (C, H, and N) and were characterized by standard methods (infrared and visible spectroscopy and magnetic susceptibility measurements).

Cyclic Voltammetry. Measurements were made with a Princeton Applied Research Model 174A polarographic analyzer equipped with a Houston Model 9002 A *X-Y* recorder and utilizing a three-electrode geometry. The working electrode was a Beckman platinum button and the auxiliary electrode was either a Beckman platinum flag or a coil of Pt wire. The standard calomel reference electrode was separated from the bulk of the solution by a NaCl-agar salt bridge with a medium glass frit.

The reliability of the electrochemical data was periodically checked by measuring the oxidation potential of a 2.0×10^{-3} M Me_2SO solution of sublimed ferrocene. A peak potential (E_p) value of +0.502

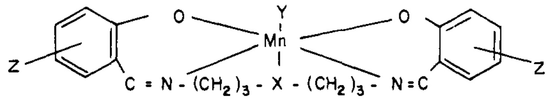
Table II. Cyclic Voltammetry Data for the Mn(III) → Mn(II) Reduction: Central Donor Effect and Anion Effect

complex	concn, M	ν, mV/s	E_{p_c}, V	E_{p_a}, V	ΔE, mV	i_{p_c}, μA	i_{p_c}/i_{p_a}
Mn(SALDPT)NO_2	1.0×10^{-3}	2	−0.255	−0.164	91	2.8	1.03
		5	−0.264	−0.155	109	4.2	1.07
		10	−0.271	−0.148	123	5.7	1.07
		20	−0.285	−0.135	150	7.9	1.11
Mn(SALDPT)Br·H_2O	1.0×10^{-3}	2	−0.241	−0.173	68	3.1	0.97
		5	−0.243	−0.173	70	4.6	1.00
		10	−0.246	−0.171	75	6.5	0.98
		20	−0.248	−0.167	81	8.9	1.00
Mn(SALMeDPT)NCS	1.0×10^{-3}	2	−0.267	−0.188	79	3.2	1.00
		5	−0.272	−0.184	88	5.1	1.02
		10	−0.279	−0.179	100	7.2	1.10
		20	−0.285	−0.170	115	9.9	1.12
	5.0×10^{-4}	2	−0.267	−0.185	82	1.8	1.08
		5	−0.273	−0.181	92	2.8	1.10
		10	−0.280	−0.175	105	3.8	1.09
		20	−0.268	−0.168	188	5.2	1.12
Mn(SALPrDPT)I	1.0×10^{-3}	2	−0.260	−0.192	68	2.7	1.03
		5	−0.262	−0.190	72	4.1	1.05
		10	−0.265	−0.187	78	5.7	1.07
		20	−0.270	−0.183	87	7.9	1.09
Mn(SALDAPE)NCS	1.0×10^{-3}	2	−0.167	−0.092	75	3.0	1.05
		5	−0.166	−0.092	74	4.7	1.08
		10	−0.167	−0.091	76	6.4	1.09
		20	−0.169	−0.088	81	9.1	1.14

± 0.005 V was observed at slow scan rates (2 or 5 mV/s) with a ΔE value of 73 ± 3 mV. Potential values reported herein are thus believed to be accurate to within ± 0.005 V for these scan rates but no better than ±0.01 V at scan rates faster than 10 mV/s. The ratio of the current at the cathodic peak potential (i_{p_c}) to that of the anodic peak potential (i_{p_a}) was determined as suggested by Adams.[11] After scanning well past the cathodic peak (~0.200-0.300 V), the potential was held constant and the current allowed to decay to a steady value before initiating the anodic scan. In this manner, reliable base lines for the anodic current could be obtained.

Results and Discussion

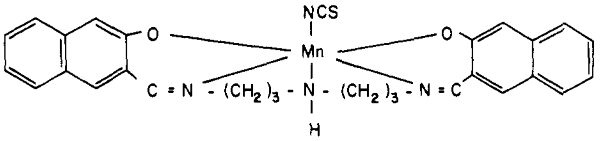
Manganese(III) complexes employing pentadentate ligands (structures I and II) derived from various substituted salicylaldehydes and symmetrical linear polyamines which differ in the central donor group have been studied electrochemically employing cyclic voltammetry. Thiocyanate principally served as the counteranion but a nitrate, bromide, and iodide complex were also investigated. Dimethyl sulfoxide (Me_2SO) was used as the solvent for this work.



I

X = NH, Mn(ZSALDPT)Y
X = NCH_3; Mn(ZSALMeDPT)Y
X = NC_3H_7; Mn(ZSALPrDPT)Y

Y = I^-, Br^-, NO_2^-, NCS^-
Z = H, 5-NO_2, 3-NO_2, 5-CH_3, 3-CH_3O, 5-CH_3O, 5-Cl
X = O; Mn(ZSALDAPE)Y



II, Mn(NAPDPT)NCS

The cyclic voltammetry data obtained for the Mn(III) → Mn(II) reduction of the complexes in Me_2SO are presented in Tables I and II. Other ill-defined and/or irreversible reductions were also observed cathodic to −1.3 V in a few of the complexes. No reversible or quasi-reversible oxidations were observed for any of the complexes. The one I^- complex (Table II), however, did yield an irreversible oxidation of I^- at +0.12 V. Several main areas that bear discussing regarding the data in Tables I and II 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 pentadentate ligand, and (4) the dependency of the reduction on the counterion.

The cyclic voltammogram of Mn(5-CH_3OSALDPT)NCS is illustrated in Figure 1 as a typical example of the reduction and subsequent oxidation of the complexes. As indicated in Table I, the reduction and subsequent oxidation of the complexes are assigned to the one-electron transfer Mn(III) + e $\rightleftharpoons$ Mn(II). The reduction waves reported are not observed in the free ligand $H_25NO_2SALDPT$ and those reductions attributable to the ligand itself are also observed in the complex. Thus the assignment of the reduction to Mn(III) → Mn(II) is reasonably straightforward, although it is likely that the electron enters a molecular orbital with some ligand contribution. A truly reversible 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. For all of the complexes reported in Table I, 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 vs. the square root of the scan rate at fixed concentrations (Figure 2) and i_p vs. concentration at fixed scan rates (Figure 3) are linear. These findings indicate that the electron transfer reactions are of the quasi-reversible type.

With regard to substituent effects, it is known that electron-withdrawing substituents enhance the rate of nucleophilic aromatic substitution;[12] that is, groups such as -NO_2 stabilize the increased electron density donated by the nucleophile to the aromatic ring. If the substituents exert any effect on the reduction (addition or reduction of electron density) of the Mn(III) to Mn(II) then the reduction process for an elec-

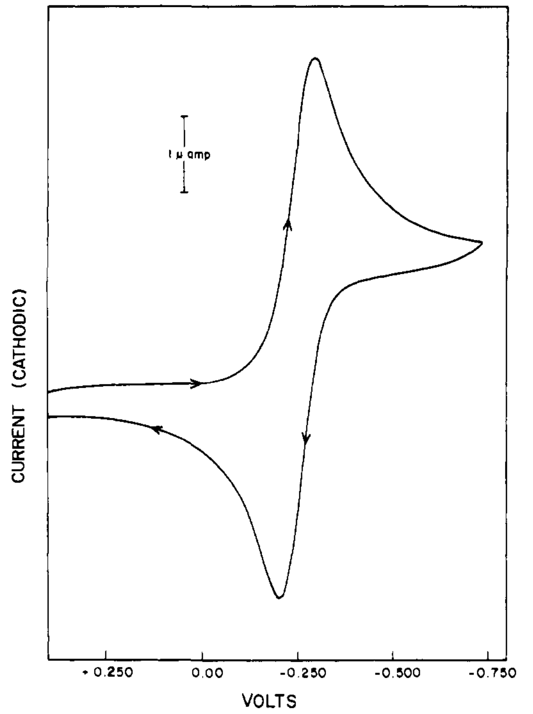


Figure 1. Cyclic voltammogram for Mn(5-CH_3OSALDPT)NCS. Scan rate = 5 mV/s, concentration = 10^{-3} M.

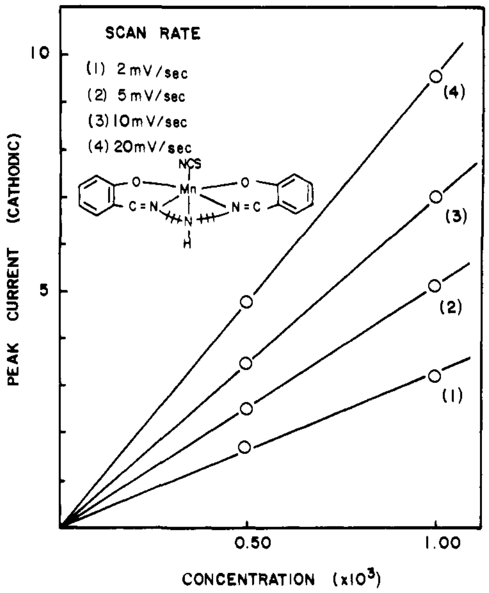


Figure 2. Cathodic peak current vs. concentration for Mn(SALDPT)NCS at various scan rates.

tron-withdrawing substituent should be favored relative to an electron-donating substituent. By comparing the E_p values of different complexes at identical scan rates, concentrations, and anion, it is seen in this study that this is indeed the case. The data are summarized by Figure 4.

As can be seen, electron-withdrawing groups such as $-NO_2$ or -Cl exhibit E_p values anodic to those with electron-donating groups such as $-CH_3$ or $-OCH_3$. The E_p value for Mn(SALDPT)NCS, which contains no strong electron-donating or -withdrawing substituent, lies in between the extremes, thus lending additional support for a substituent effect. One can also observe that, where comparisons are possible, a group in the 5 position causes a larger shift than the same group in the 3 position. For example, Mn(5-NO_2SALDPT)NCS has a reduction potential more anodic than Mn(3-NO_2SALDPT)NCS while Mn(5-CH_3OSALDPT)NCS had a reduction potential more cathodic than Mn(3-MCH_3O-SALDPT)NCS. Fusion of an aromatic six-membered ring to yield Mn(NAPDPT)NCS (structure II) is observed to offer the greatest stability for Mn(III) of the complexes studied here.

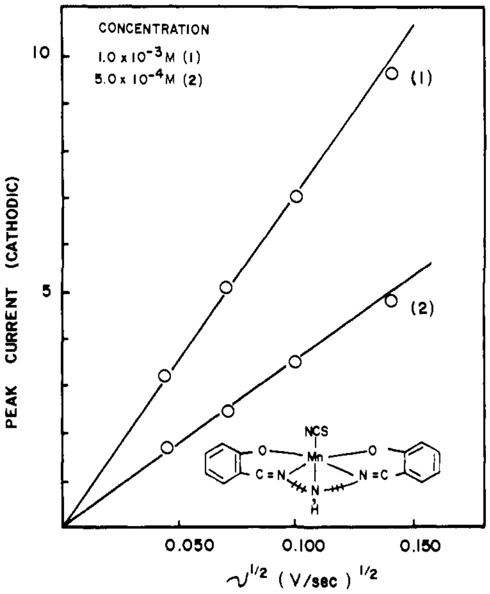


Figure 3. Cathodic peak current vs. the square root of the scan rate for Mn(SALDPT)NCS.

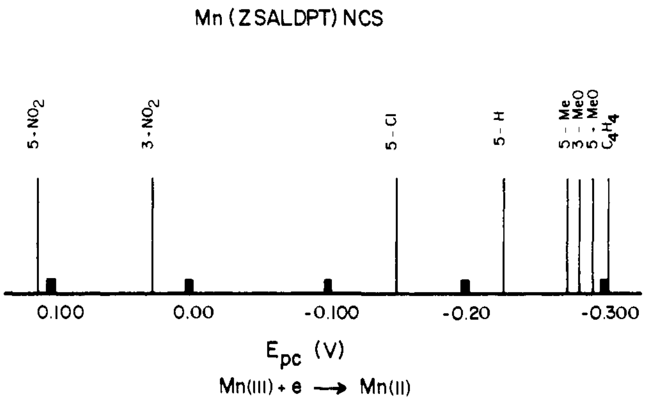


Figure 4. Relative peak positions for Mn(III) → Mn(II) reduction for Mn(ZSALDPT) NCS complexes in Me_2SO.

Unique effects are also observed when the proton of the DPT backbone is replaced with a CH_3 group yielding MeDPT complexes. As alkyl groups normally enhance the basicity of the nitrogen in alkylamines, one would expect the Mn(III) to Mn(II) reduction to be less favored and hence cathodic for Mn(SALRDPT)X compared to Mn(SALDPT)X. The data (Table II) also confirm this as the E_p values for Mn(SALMeDPT)NCS and Mn(SALPrDPT)I are cathodic to that of Mn(SALDPT)X. In a like manner, when the NR group is replaced with a less basic donor such as an ether oxygen atom as in Mn(SALDAPE)NCS (Figure 5) the reduction is shifted in an anodic direction relative to Mn(SALDPT)NCS. It therefore appears that the more electron donating the ligand, which may come about by incorporating a better donor into the ligand or by selective substitution on the aromatic ring, the more accessible is the Mn(III) oxidation state. It is somewhat surprising that rather subtle changes on the aromatic ring of the ligand with identical donors can give rise to relatively large differences in E_p (i.e., E_{p_c} = +0.110 V for Mn(5-NO_2SALDPT)NCS vs. E_{p_c} = −0.290 V for Mn(5-CH_3O-SALDPT)NCS) for Mn(III) → Mn(II).

Table II also contains data in which the anion has been varied and other conditions have been held constant. Changes in the anion have been shown to alter the reduction potential of a series of Mn(III) porphyrins.[13] Conductivity data of these complexes in Me_2SO ($\Lambda m \sim 50$ cm^2 Ω^{-1} mol^{-1}; concn = 1 mM) show them to be 1:1 electrolytes[14] indicating that a Me_2SO molecule has replaced the anion in the coordination sphere of the Mn(III) and thus the anion effect should be minimal. There does appear to be a very slight anion effect which is consistent with the spectrochemical series in that the E_p values are in the order Br^-, NCS^-, NO_2^- with NO_2^- having the most cathodic peak potential ligand.

Correlation with Dioxygen and Nitric Oxide Reactivity. The observed relatively low, and in some cases positive, reduction potentials for these Mn(III) complexes compare very well with their ease of reduction with nitric oxide, hydrogen peroxide, or superoxide ion to Mn(II) complexes.[7] However, at this point it is most interesting to speculate with the information gathered here concerning the relationship observed between reactivity with dioxygen and nitric oxide and the complementary set of Mn(II) complexes.[4,5]

When the Mn(II) complexes react with nitric oxide the product isolated is a Mn(I) nitrosyl.[5] Those complexes with electron-donating substituents, 3-CH_3O and 5-CH_3, formed red nitrosyl complexes in solution; however, the NO was lost during isolation, leaving a bright yellow solid characterized as the Mn(II) percursor. In contrast, those complexes with H or an electron-withdrawing group, 5-NO_2, yield stable Mn(I) nitrosyls which have been well characterized.[5] The stability of the Mn-NO link is related to the accessibility of the Mn(I) state, which is enhanced by an electron-withdrawing group and conversely hindered by an electron-donating group. Hence, the observed trend in redox properties seen here is complemented by the NO reactivity of these complexes and subsequent nitrosyl product stability.

With regard to dioxygen reactivity, it was found that electron-donating groups promoted extensive oxidation (i.e., manganese and ligand) whereas electron-withdrawing groups showed only manganese oxidation. With the information presented here it seems that the electron-donating substituents could possibly render the complex susceptible to further oxidation either through increased electron density on the ligand or through stabilization of a catalytic amount of Mn(IV). In contrast, electron-withdrawing groups would tend to reduce both of the above possibilities. Unfortunately, the Me_2SO solvent system precluded our study of Mn(III) to Mn(IV) with these complexes.

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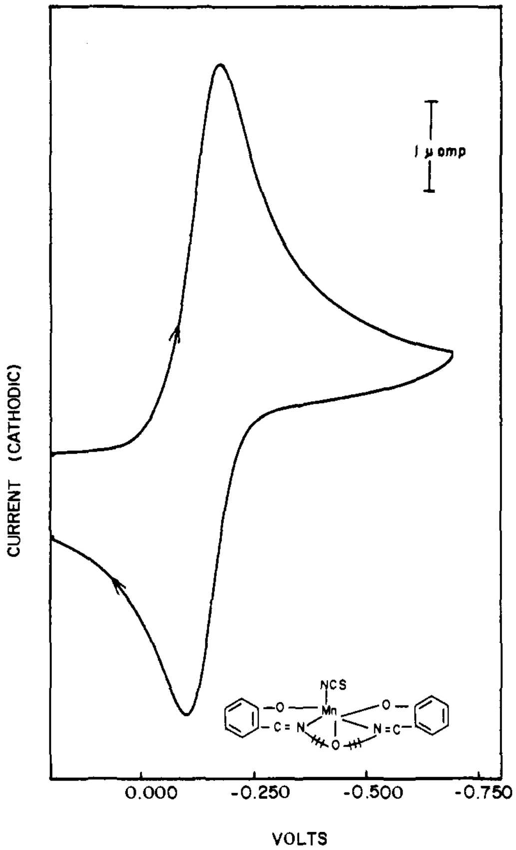

Figure 5. Cyclic voltammogram for Mn(SALDAPE)NCS. Scan rate = 5 mV/s, concentration = 10^{-3} M.

References and Notes

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