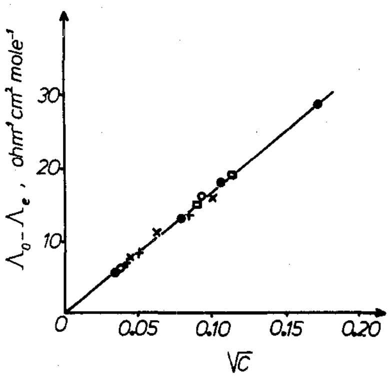


Figure 1. Plot of $\Lambda_0 - \Lambda_e$ vs. $c^{1/2}$ for $[Co(NO)_2L_2]^+PF_6^-$ samples: L = MeCN (•), AN (○), Λ_0 = 97 Ω^{-1} cm^2 mol^{-1}; L = COD (×), Λ_0 = 92 Ω^{-1} cm^2 mol^{-1}; L = NBD (+), Λ_0 = 88 Ω^{-1} cm^2 mol^{-1}; L = PhCN (□), Λ_0 = 77 Ω^{-1} cm^2 mol^{-1}.

chromium,[21] molybdenum,[22] and nickel[17] complexes: the diolefin ligands are bonded as chelates with loss of the olefinic character.

Conductometric Measurements with $[Co(NO)_2L_2]^+PF_6^-$ Complexes. Conductances have been measured in order to determine the complex electrolyte types. The best method was to carry conductometric measurements over concentrations covering the range 2×10^{-4}–3×10^{-2} M. This method allows application of the Onsager law in the form $\Lambda_0 - \Lambda_e = Bc^{1/2}$ where the equivalent conductance Λ_e plotted against $c^{1/2}$ provides a straight line extrapolated to zero concentration to obtain Λ_0 as the intercept. The slope B is characteristic of the electrolyte and direct comparison of values obtained for different cations is available since the anion remains the same.[23] Figure 1 reports the variations of $\Lambda_0 - \Lambda_e$ vs. $c^{1/2}$ for $[Co(NO)_2L_2]^+PF_6^-$ compounds (L = MeCN, PhCN, AN, NBD, COD). The experimental values fit very nicely with the same straight line. This result indicates that dinitrosylcobalt complexes have identical behaviors. The Λ_0 values fall within the range 77–97 Ω^{-1} cm^2 mol^{-1} and the slope B is equal to 167. These data are typical of 1:1 electrolytes in nitromethane[24] and agree with those of other cationic nitrosylcobalt complexes.[25]

Characterization of $[Co(NO)_2L_2]^+Y^-$ (L = MeCN, PhCN, Y^- = BF_4^-, ClO_4^-). The tetrafluoroborate anion exhibits absorption bands centered at ca. 1000 and 525 cm^{-1} consistent with T_d symmetry.[10] The perchlorate anion has similar properties with absorption maxima at 1095 and 630 cm^{-1}.[26] The noncoordinating interaction has not always been observed. Ibers et al.[27] have characterized by x-ray analysis and vibrational spectroscopy a C_{3v} symmetry of the BF_4^- moiety in the complex $Cu(PPh_3)BF_4$ denoting a Cu–FBF_3 interaction which is described as a weak coordination. A similar situation has been depicted for the compound $Pt(C_6F_5)(PEt_3)ClO_4$.[28] Infrared and conductometric measurements lead us to assume a platinum–oxygen interaction.

Table II reports stretching frequencies of nitrosyl and nitrile groups. In comparison with data on complexes **2** and **3** no significant effect is seen to arise when the hexafluorophosphate anion is replaced by the tetrafluoroborate or perchlorate anion. Thus we can conclude that in this study the three counteranions are not coordinated.

Acknowledgment. Acknowledgment is made to the Société Nationale Elf Aquitaine which has permitted us to undertake and publish this work. The authors wish to thank Mr. Mozzanega for skilled laboratory assistance in the synthesis of samples for elemental analysis.

Registry No. **1**, 13931-93-6; **2**, 61505-89-3; **3**, 61505-91-7; **4**, 61505-93-9; **5**, 61505-95-1; **6**, 61505-97-3; **7**, 61508-65-4; **8**, 61558-17-6; **14**, 61505-98-4; **15**, 61505-99-5; **16**, 61528-38-9; **17**, 61506-00-1; $[Co(NO)_2(PPh_3)_2]^+ClO_4^-$, 24504-01-6; $[Co(NO)_2(PPh_3)_2]^+PF_6^-$, 37739-55-2; $[Co(NO)_2(PPh_3)_2]^+BF_4^-$, 24507-62-8.

References and Notes

(1) (a) N. G. Connelly, *Inorg. Chim. Acta*, **6**, 47 (1972); (b) B. F. G. Johnson and J. A. McCleverty, *Prog. Inorg. Chem.*, **7**, 277 (1966); (c) W. P. Griffith, *Adv. Organomet. Chem.*, **7**, 211 (1968); (d) B. A. Frenz and J. A. Ibers, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One*, **11**, 33 (1972); (e) C. B. Ungermann and K. G. Caulton, *J. Am. Chem. Soc.*, **98**, 3862 (1976); (f) M. Di Vaira, C. A. Ghilardi, and L. Sacconi, *Inorg. Chem.*, **15**, 1555 (1976); (g) R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, **8**, 26 (1975).

(2) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974);

(3) (a) J. P. Candlin and W. H. Janes, *J. Chem. Soc. C*, 1856 (1968); (b) P. L. Maxfield, U.S. Patent 3 377 397 (Oct 22, 1965); (c) I. Tkatchenko, German Patent 2 417 985 (April 12, (1973); (d) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Am. Chem. Soc.*, **91**, 5659 (1969); (e) E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *ibid.*, **92**, 528 (1970); (f) S. T. Wilson and J. A. Osborn, *ibid.*, **93**, 3068 (1971).

(4) D. Ballivet and I. Tkatchenko, *J. Mol. Catal.*, **1**, 322 (1976).

(5) A. Sacco, M. Rossi, and C. F. Nobile, *Ann. Chim. (Rome)*, 499 (1967).

(6) T. Bianco, M. Rossi, and L. Uva, *Inorg. Chim. Acta*, **3**, 443 (1969).

(7) W. Hieber and H. Führling, *Z. Anorg. Allg. Chem.*, **373**, 48 (1970).

(8) W. Hieber and K. Heinicke, *Z. Anorg. Allg. Chem.*, **316**, 305 (1962).

(9) D. Gwost and K. G. Caulton, *Inorg. Chem.*, **12**, 2095 (1973).

(10) D. Ballivet, C. Billard, and I. Tkatchenko, *J. Organomet. Chem.*, **124**, C7 (1977).

(11) P. W. Jolly, F. G. A. Stone, and K. Mackenzie, *J. Chem. Soc.*, 6416 (1965).

(12) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, N.Y., 1963.

(13) B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, **14**, 3060 (1975).

(14) (a) D. H. Payne, Z. A. Payne, R. Rohmer, and H. Frye, *Inorg. Chem.*, **12**, 2540 (1973); (b) P. C. Ford and R. E. Clarke, *Chem. Commun.*, 1109 (1968); (c) W. R. McWhinnie, J. D. Miller, J. B. Watts, and D. Y. Waddan, *J. Inorg. Nucl. Chem.*, **37**, 2329 (1975); (d) E. D. Sherman and P. R. Schreiner, *J. Chem. Soc., Chem. Commun.*, 3 (1976); (e) J. E. Sutton and J. I. Zink, *Inorg. Chem.*, **15**, 675 (1976); (f) J. M. Bellerby and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 1281 (1975); (g) T. Tatsumi, M. Hidai, and Y. Uchida, *Inorg. Chem.*, **14**, 2530 (1975); (h) J. L. Thomas, *J. Am. Chem. Soc.*, **97**, 5943 (1975).

(15) R. C. de Lanson, H. Zon-Hong, G. J. Jordan, F. P. Schinco, and C. A. Maciorowski, *J. Am. Chem. Soc.*, **96**, 4932 (1974).

(16) G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5310 (1959).

(17) C. A. Tolman and W. C. Seidel, *J. Am. Chem. Soc.*, **96**, 2774 (1974); C. A. Tolman, *ibid.*, **96**, 2780 (1974).

(18) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1969, p 1112.

(19) (a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951); (b) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(20) D. A. Edwards and R. Richards, *J. Organomet. Chem.*, **86**, 407 (1975).

(21) G. Platbrood and L. Wilputte-Steinert, *J. Organomet. Chem.*, **85**, 199 (1975).

(22) I. A. Garbuzova, V. T. Aleksanyan, and M. A. Pryanishnikova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1675 (1973).

(23) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

(24) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

(25) R. D. Feltham and R. S. Nyholm, *Inorg. Chem.*, **4**, 1334 (1965).

(26) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

(27) A. P. Gaughan, Z. Dori, and J. A. Ibers, *Inorg. Chem.*, **13**, 1657 (1974).

(28) R. Uson, P. Royo, and J. Gimeno, *J. Organomet. Chem.*, **72**, 299 (1974).

(29) W. Beck and K. Lottes, *Chem. Ber.*, **98**, 2657 (1965).

Contribution from the Department of Chemistry,
Syracuse University, Syracuse, New York 13210

Electrochemical Redox Behavior of a Series of Manganese Macrocyclic Complexes

Francis C. McElroy, James C. Dabrowiak,*
and Daniel J. Macero*

Received July 26, 1976 AIC605215

The redox behavior of transition metal complexes containing synthetic macrocyclic ligands has received considerable attention.[1-6] In an attempt to ascertain and characterize the various oxidation states of manganese possible when this element is coordinated with certain synthetic macrocyclic structures, we investigated the electrochemical properties of a series of manganese complexes of the type $[Mn^{III}L^{2-}X$-

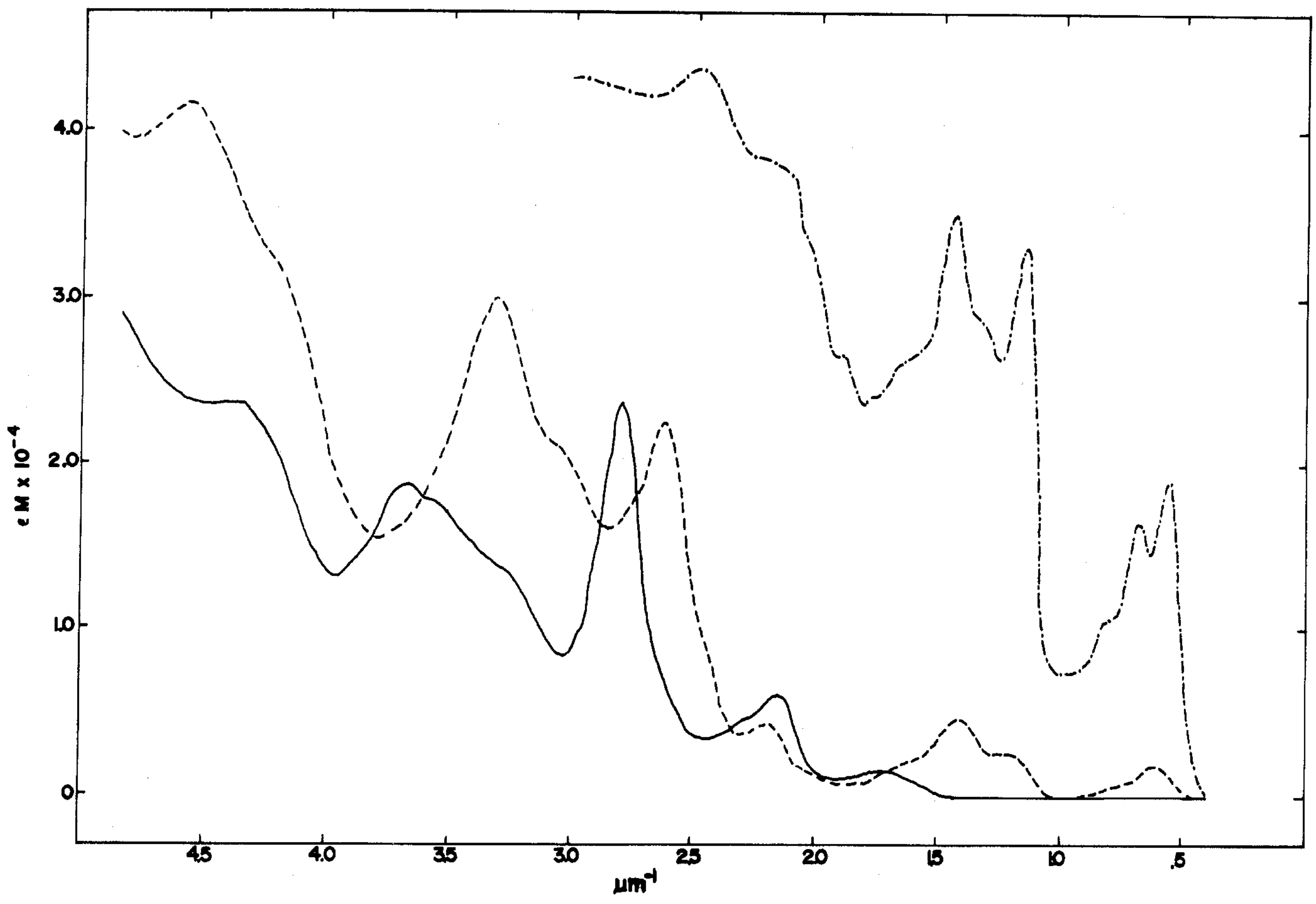
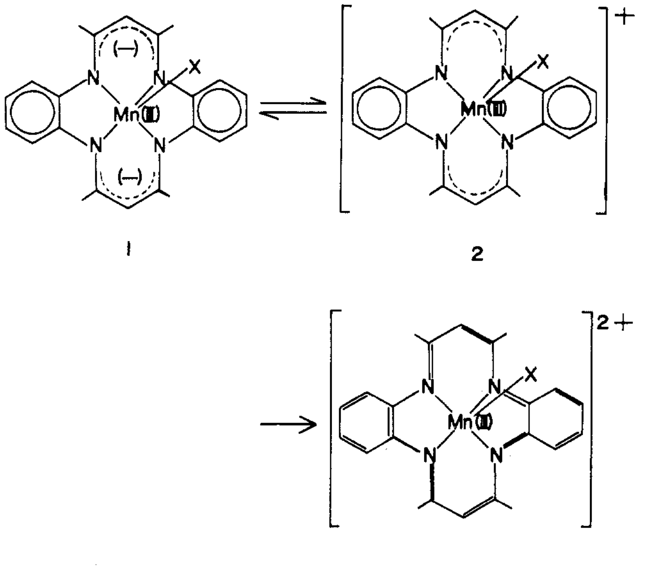


Figure 1. Visible absorption spectra of $[Mn^{III}L^{2-}Cl(24\pi)]$ (—) and $[Mn^{III}L^{-}\cdot Cl(23\pi)]PF_6$ (- - -) in purified acetonitrile solution and the solid-state mull spectrum of $[Mn^{III}L^{-}\cdot Cl(23\pi)]PF_6$ at 77 K (- · · · ·).

$(24\pi)]^0$, where X is Cl^-, Br^-, SCN^-, and N_3^-, **1**. From a combination of electrochemical and other physical techniques we have established that the first one-electron oxidation product of $[Mn^{III}L^{2-}Cl(24\pi)]^0$ is the monomeric π cation radical compound $[Mn^{III}L^{-}\cdot Cl(23\pi)]^+$, **2**. Since the manganese complexes sustain a second one-electron oxidation, they appear to be members of a two-electron-transfer series which culminates in the formation of the Hückel aromatic structure $[Mn^{III}L^0X(22\pi)]^{2+}$, **3**. Although this oxidation behavior sharply contrasts with that observed for $[Ni^{II}L^{2-}]$ (oxidation leads to the formation of a dimeric structure),[6] it is in accord with that found for other antiaromatic macrocyclic structures.[4]



1

2

3

Experimental Section

Physical Measurements. UV–visible absorption spectra of solutions of $[Mn^{III}L^{-}\cdot Cl(23\pi)]PF_6$ and $[Mn^{III}L^{2-}Cl(24\pi)]^0$ in purified spectral grade acetonitrile were obtained with a Cary 118-C or Cary 14 spectrophotometer from 0.4 to 4.5 μm^{-1}. The spectrum of the solid-state mull of the oxidized product was obtained at 77 K. The respective absorption spectra are shown in Figure 1. Infrared spectra of Nujol mulls of the compounds were taken with a Model 521 Perkin-Elmer spectrometer.

The ESR properties of $[Mn^{III}L^{2-}Cl(24\pi)]^0$ and its one-electron oxidation and reduction products in purified acetonitrile[7] solution were determined at room temperature with a Varian E-9 (X-band, 9.4-GHz) spectrometer. The magnetic field strength was varied from 500 to 6500 G. In addition, ESR spectra of $[Mn^{III}L^{2-}Cl(24\pi)]^0$ and its one-electron oxidation product, $[Mn^{III}L^{-}\cdot Cl(23\pi)]PF_6$, were taken at 77 and at 5.2 K in both acetonitrile solution and in the solid state. No ESR transitions could be observed for either of the last two compounds. The ESR parameters determined for the one-electron reduction product of $[Mn^{III}L^{2-}Cl(24\pi)]$ are given below. A Faraday balance, calibrated with $HgCo(SCN)_4$,[8] was used to measure the magnetic susceptibility of $[Mn^{III}L^{-}\cdot Cl(23\pi)]PF_6$ over a temperature range of 81–352 K. The diamagnetic correction determined for the macrocyclic ligand H_2L was -215×10^{-6} cgsu. The observed magnetic data for $[Mn^{III}L^{-}\cdot Cl(23\pi)]PF_6$ were as follows [T, K (χ_M, 10^{-6} cgsu)]: 352 (5743), 323 (6246), 294 (6748), 249 (8173), 236 (8639), 206 (9881), 183 (11 114), 149 (13 718), 101 (20 130), 81 (24 606). A plot of $1/\chi_M$ vs. absolute temperature was linear with $\Theta = 0 \pm 5$ K.

Conductance measurements were made with an Industrial Instruments, Inc., Model RC-18 conductance bridge and carried out in degassed, purified acetonitrile[7] at 25.00 ± 0.01 °C. The conductivity cell was calibrated with 0.01 N KCl. A linear plot was obtained for the variation of equivalent conductance with $c^{1/2}$ over the range 1.01×10^{-4} to 1.39×10^{-3} M with Λ_0 found to be 155 $cm^2\ \Omega^{-1}\ equiv^{-1}$.

Table I. Voltammetric Data for the Manganese Complexes $[Mn^{III}L^{2-}X(24\pi)]^0$

Axial anion, X^-	Complex couple	Dc polarography[a]	Cyclic voltammetry[b]	Ac polarography[c]
Cl^-	1+ 2+	+1.28 (+84)	NRP[d] (115)	f
	0 1+	+0.562 (+63)	60[d] (115)	93[d]
	1– 0	–0.681 (–59)	70[e] (100)	94[e]
Br^-	1+ 2+	+1.02 (+178)	NRP[d] (93)	f
	0 1	+0.578 (+65)	62[d] (93)	95[d]
	1– 0	–0.665 (–70)	75[e] (102)	97[e]
NCS^-	1+ 2+	+1.20 (+82)	NRP[d] (68)	f
	0 1+	+0.635 (+69)	80[d] (68)	110[d]
	1– 0	–0.658 (–61)	70[e] (100)	105[e]
N_3^-	2+ 3+	+1.07 (+83)	NRP[d] (75)	f
	1+ 2+	+0.67 (+123)	200[d] (75)	f
	0 1+	+0.39 (+106)	130[d] (75)	160[d]
	0 1+	+0.315 (+51)	100[e] (64)	160[e]
	1– 0	–0.720 (–55)	75[e] (103)	95[e]

[a] The $E_{1/2}$ is given in V followed by the slope in mV in parentheses. All potentials are referenced vs. the Ag/AgCl/saturated NaCl electrode. [b] The aniodic–cathodic peak splitting is given in mV followed by the cyclic voltammetry scan time in mV/s in parentheses. NRP is no reverse peak. [c] The width at half-height of the wave is given in mV at 30 Hz. [d] Pt. [e] Hg. [f] Ac widths greater than 200 mV.

The observed and calculated slopes for Et_4NBF_4 were 345 and 373; those for $[Mn(III)L^{-}\cdot Cl(23\pi)]PF_6$ were 330 and 344, respectively.[9]

Dc polarograms and cyclic voltammograms (CV) were obtained on an instrument described earlier.[10] In-phase ac polarograms were obtained with the aid of a Princeton Applied Research Model 121 lock-in amplifier. Positive *IR* compensation was employed where necessary and a Hewlett-Packard Model 7001-A X-Y recorder was used to obtain permanent records of the polarographic traces. A conventional polarographic H-cell was used as the electrolysis vessel. An aqueous Ag/AgCl/saturated NaCl reference electrode was isolated from the background solution by a medium-porosity glass frit. Solutions were prepared in situ by first degassing the acetonitrile solution containing 0.1 M Et_4NBF_4 with dry nitrogen for 30 min and then dissolving 5–10 mg of the complex in the solution. All voltammetric measurements were carried out at room temperature, 24 ± 2 °C.

Preparation of the Complexes. The preparation of the ligand,[11] H_2L, and the manganese(III) complexes[12] has been previously reported. The compound $[Mn^{III}L^{-}\cdot Cl(23\pi)]PF_6$, **2**, was prepared electrochemically under dry nitrogen. A solution of $[Mn^{III}L^{2-}Cl(24\pi)]^0$, **1** (140 mg dissolved in 200 mL of purified Spectrograde acetonitrile),[7] containing 0.1 M electrolyte, $(n\text{-}Bu)_4NPF_6$, was electrolyzed completely at an applied constant potential of 0.80 V vs. the Ag/AgCl reference electrode. A dark green, moisture-sensitive solid resulted. This product was filtered, washed with a few milliliters of purified acetonitrile, and dried under a stream of dry nitrogen. The yield was approximately 30 mg. Anal. Calcd for $C_{22}H_{22}N_4ClMnPF_6$: C, 45.73; H, 3.84; N, 9.70; Cl, 6.14; Found: C, 45.42; H, 3.88; N, 9.69; Cl, 6.12. IR spectrum (Nujol): 1562 (s), 1535 (w), 1304 (m), 1201 (m), 761 (s), 747 (m) cm^{-1}. UV–vis spectrum in CH_3CN [μm^{-1}, (ϵ_M)]: 0.551 sh, 0.595 (1900), 0.714 sh, 1.20 sh, 1.43 (6120), 1.67 sh, 2.02 sh, 2.19 (5300), 2.65 (23 600), 2.77 sh, 3.08 sh, 3.33 (30 500), 4.26 sh, 4.59 (42 600). Solid-state spectrum at 77 K: (μm^{-1}): 0.560, 0.690, 8.33 sh, 1.16, 1.45, 2.22 sh, 2.50.

Results and Discussion

Table I summarizes the electrochemical results obtained for the complexes. Except for the azide derivative, the various manganese(III) complexes had similar electrochemical behavior. Each compound showed two one-electron oxidation waves, the first being reversible and the second somewhat irreversible. The oxidation waves are most likely associated with the formation of structures **2** and **3**. The azide complex exhibited electrochemical behavior which was different from that of the others. For this compound reproducible results could only be obtained by pretreating the electrode before each run; however, in either case the waves were quasi-reversible or irreversible. It should be noted that when the 0 → 1+ oxidation couple was observed on both a mercury and a platinum electrode, there was a substantial difference in the respective half-wave potentials which indicates that surface effects play an important role in the electrode process.

In an effort to determine the site within the complex which has undergone the oxidation process (ligand or metal ion), the first one-electron oxidation product of $[Mn^{III}L^{2-}Cl(24\pi)]^0$ was electrochemically generated and characterized. Chemical analysis and conductivity data show that the oxidation product is monomeric and yields a 1:1 electrolyte in solution. The solid-state IR data for this compound and its reduced parent, $[Mn^{III}L^{2-}Cl(24\pi)]^0$, are very similar; however, the oxidized species exhibits a strong band at 1562 cm^{-1} and a weaker absorption at 1535 cm^{-1}. This band pattern is not found in the IR spectrum of the parent compound or in the spectra of any M(II)–M(III) derivatives with the 24π macrocyclic Schiff base ligand.[6,12,13] This observation suggests that the ligand framework, specifically the diiminate portion, has been modified in the oxidation and that the product is best formulated as $[Mn^{III}L^{-}\cdot Cl(23\pi)]^+$. Oxidation of the diiminate portion of this macrocyclic Schiff base ligand has been previously established.[6]

Figure 1 shows the absorption spectra for $[Mn^{III}L^{2-}Cl(24\pi)]^0$ and its oxidation product. Unlike any of the reported M(II)–M(III) complexes with this ligand,[12–15] $[Mn^{III}L^{-}\cdot Cl(23\pi)]^+$ exhibits strong bands in the near-infrared region at ~0.6 μm^{-1}. The intensity of these bands suggests that they are associated with either electronic transitions localized on the modified ligand framework itself or are charge transfer in origin. Similar spectral behavior has been noted for oxidized metalloporphyrins which contain a complexed ligand radical.[3,16]

The magnetic properties of $[Mn^{III}L^{-}\cdot Cl(23\pi)]^+$ are typical of those found for a porphyrin π cation radical complex.[16] The oxidized Schiff base complex is paramagnetic but ESR inactive.[17] This type of behavior has been observed for $[Mn^{III}OEP(OH)]^+$, $[Cu^{II}TPP]^+$, and $[Fe^{III}TPP(OAC)]^+$ [2,3,18] all of which contain a ligand radical complexed to a paramagnetic metal ion. On the other hand, if the oxidation product were $[Mn^{IV}L^{2-}Cl(24\pi)]^+$, the complex should be ESR active. Numerous Cr(III) complexes and a few well-documented Mn(IV) compounds exhibit ESR spectra at room temperature or at 77 K.[19]

The observed magnetic moment for the compound is 4.01 μ_B and temperature invariant.[20] In view of the preceding discussion the moment must be the result of strong antiferromagnetic coupling between the d^4 metal ion and the complexed ligand radical. The observation that the moment is invariant with temperature implies that the ferromagnetic state ($S = {}^5/_2$) lies far above (>1000 cm^{-1}) the antiferromagnetic level ($S = {}^3/_2$). Both ferro- and antiferromagnetic porphyrin analogies exist[3] but their variable temperature magnetic behavior has not yet been reported.

Finally, the cationic complex $[Mn^{III}L^{-}\cdot Cl(23\pi)]PF_6$ exhibits chemical behavior which is typical of a radical. The solid compound is difficult to keep, even under dry nitrogen. Over a period of weeks it slowly decomposes. The complex is sensitive to trace amounts of water. Because of this sensitivity the spectral grade acetonitrile solvent must be thoroughly dried to obtain reproducible conductance values.

Examination of Table I shows that each complex exhibits a one-electron, diffusion-controlled reduction wave corresponding to the reduction of manganese(III) to manganese(II). This redox couple is reversible when measured with ac and CV but somewhat irreversible when scanned with the slower dc polarographic technique. Constant-potential electrolysis of $[Mn^{III}L^{2-}Cl(24\pi)]^0$ at a potential of –0.9 V does not yield a stable complex. Since the reduction product is a structurally distorted, relatively unstable complex and has only been isolated as a five-coordinate tertiary amine adduct,[12,21] the irreversible behavior at slow scan rates is expected. The observed irreversibility is most likely due to the loss of chloride ion from the manganese(II) complex followed by solvation and ultimately decomposition of the solvated complex as shown in eq 1 and 2. Such behavior is consistent with the known

$$[\mathrm{Mn^{III}L^{2-}Cl(24\pi)}] \xrightarrow{+e^-} [\mathrm{Mn^{II}L^{2-}Cl(24\pi)}]^- \qquad (1)$$

$$\text{solvent} + [\mathrm{Mn^{II}L^{2-}Cl(24\pi)}]^- \rightarrow [\mathrm{Mn^{II}L^{2-}(24\pi)(solvent)}]^0 + \mathrm{Cl^-} \qquad (2)$$

solution behavior of the Mn(II) compound. A room-temperature ESR spectrum of the reduction product in CH_3CN gave a $g \approx 2$ transition having a six-line hyperfine coupling pattern. An identical ESR spectrum was observed for $[\mathrm{Mn^{II}L^{2-}(NEt_3)}]^0$ dissolved in acetonitrile at room temperature.[12]

The dianionic macrocyclic ligand L^{2-} stabilizes the trivalent oxidation state of manganese relative to the saturated macrocyclic system [14]aneN_4.[22] However, the dianionic ligand apparently does not sufficiently stabilize Mn(IV) to enable this species to be generated by electrochemical oxidation. Instead it is the ligand framework which is oxidized. Moreover, the manganese cation does not dimerize, as does the corresponding Ni(II) radical cation complex,[6] even though molecular models show that a five-coordinate manganese complex could undergo dimerization. The contrasting chemical behavior exhibited by the manganese(III) and nickel(II) complexes must be due to the different electronic effects exerted by the individual central metal ions.

In an effort to determine the oxidation states accessible to manganese as a function of ligand structure, we are continuing to examine the redox properties of manganese macrocyclic complexes.

Acknowledgment. We thank Dr. Michael C. Hughes for his assistance in the early stages of this work and the Syracuse University Department of Chemistry for its support.

Registry No. $[\mathrm{Mn^{III}L^0Cl(22\pi)}]^{2+}$, 61634-01-3; $[\mathrm{Mn^{III}L^{-}\cdot Cl(23\pi)}]\mathrm{PF_6}$, 61633-99-6; $[\mathrm{Mn^{III}L^{2-}Cl(24\pi)}]^0$, 56943-19-2; $[\mathrm{MnLCl}]^-$, 61634-04-6; $[\mathrm{Mn^{III}L^0Br(22\pi)}]^{2+}$, 61634-03-5; $[\mathrm{Mn^{III}L^{-}\cdot Br(23\pi)}]^+$, 61634-02-4; $[\mathrm{Mn^{III}L^{2-}Br(24\pi)}]^0$, 56943-20-5; $[\mathrm{MnLBr}]^-$, 61634-06-8; $[\mathrm{Mn^{III}L^0NCS(22\pi)}]^{2+}$, 61634-05-7; $[\mathrm{Mn^{III}L^{-}\cdot NCS(23\pi)}]^+$, 61634-08-0; $[\mathrm{Mn^{III}L^{2-}NCS(24\pi)}]^0$, 56943-21-6; $[\mathrm{MnLNCS}]^-$, 61634-07-9; $[\mathrm{MnLN_3}]^{3+}$, 61634-10-4; $[\mathrm{Mn^{III}L^0N_3(22\pi)}]^{2+}$, 61634-09-1; $[\mathrm{Mn^{III}L^{-}\cdot N_3(23\pi)}]^+$, 61634-00-2; $[\mathrm{Mn^{III}L^{2-}N_3(24\pi)}]^0$, 56943-23-8; $[\mathrm{MnLN_3}]^-$, 61634-11-5.

References and Notes

(1) F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974).

(2) J. Furhop, K. M. Kadish, and D. G. Davis, *J. Am. Chem. Soc.*, **95**, 5140 (1973).

(3) A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).

(4) T. J. Truex and R. H. Holm, *J. Am. Chem. Soc.*, **94**, 4529 (1972).

(5) R. H. Felton, G. S. Owen, D. Dolphin, and J. Fajer, *J. Am. Chem. Soc.*, **93**, 6332 (1971).

(6) F. C. McElroy and J. C. Dabrowiak, *J. Am. Chem. Soc.*, **98**, 7172 (1976).

(7) T. Osa and T. Kuwana, *J. Electroanal. Chem.*, **22**, 389 (1969).

(8) V. Kotovic, L. Lindoy, and D. H. Busch, *J. Chem. Educ.*, **49**, 117 (1972).

(9) The conductivity measurements were analogous to those made in ref 4. The various constants necessary for the calculation are found in the references cited in ref 4.

(10) F. H. Fraser and D. J. Macero, *Chem. Instrum.*, **4**, 97 (1972); F. H. Fraser, Dissertation, Syracuse University, 1972.

(11) V. L. Goedken, J. Molin-Case, and Y. A. Whang, *J. Chem. Soc., Chem. Commun.*, 337 (1973).

(12) D. R. Neves and J. C. Dabrowiak, *Inorg. Chem.*, **15**, 129 (1976).

(13) D. R. Neves, M.S. Thesis, Syracuse University, 1975.

(14) W. H. Woodruff, R. Pastor, and J. C. Dabrowiak, *J. Am. Chem. Soc.*, **98**, 7999 (1976); L. A. Nafie, R. W. Pastor, J. C. Dabrowiak, and W. W. Woodruff, *ibid.*, **98**, 8007 (1976).

(15) No M(IV) derivatives with this macrocyclic ligand have yet been reported.

(16) J. Fuhrhop, "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, New York, N.Y., 1975, p 593.

(17) Attempts to obtain the ^{1}H NMR spectrum of this complex were unsuccessful. It has very limited solubility ($\sim 10^{-3}$ M) in solvents which it does not react with. Examining a saturated CH_3CN solution of the compound with an ^{1}H FT NMR spectrometer (40 000 pulses) did not result in a spectrum.

(18) OEP is octaethylporphyrin and TPP is tetraphenylporphyrin.

(19) B. R. McGarvey, *Transition Met. Chem.*, **3**, 39 (1966).

(20) This magnetic moment as well as the variable-temperature magnetic behavior is consistent with either a Mn(IV), d^3 electronic system or an antiferromagnetically coupled Mn(III) ligand radical complex.

(21) M. C. Weiss, B. Bursten, S. Ping, V. L. Goedken, *J. Am. Chem. Soc.*, **98**, 8021 (1976).

(22) P. S. Bryan and J. C. Dabrowiak, *Inorg. Chem.*, **14**, 296, 299 (1975).

Contribution from the Department of Chemistry,
Ithaca College, Ithaca, New York 14850

Thermodynamic Study of the Adduct Formation of Zinc Tetraphenylporphine with Several Neutral Donors in Cyclohexane

Glenn C. Vogel* and James R. Stahlbush[1]

Received August 11, 1976 AIC60584N

There have been numerous studies involving the Lewis acid–base interaction between metalloporphyrins and nitrogen donors.[2-9] Of these studies, several have dealt with the metalloporphyrin zinc $\alpha,\beta,\gamma,\delta$-tetraphenylporphine (ZnTPP).[5-7] Until recently, all thermodynamic studies involving the interaction of ZnTPP with various Lewis bases have used only nitrogen donors. In a recent study[10] the thermodynamic parameters for the adduct formation between ZnTPP and sulfur, oxygen, and phosphorus donors in the solvent benzene were reported. For the bases studied, the enthalpies of adduct formation increase in the order $S < O < P < N$. Since this order is the same as the order of donor strengths toward Lewis acids in which the electrostatic contribution to the bonding dominates the covalent contribution, it was proposed that ZnTPP should also fall into this category.

The enthalpy of adduct formation measured in the gas phase or poorly solvating media is a measure of the strength of the bond formed between a Lewis acid and base.[11] Since benzene is a basic solvent,[12] the interpretation of the enthalpies measured in benzene is more complex than those measured in poorly solvating media due to specific interactions between ZnTPP and benzene. In this note we report the first study of the thermodynamics of adduct formation of ZnTPP with nitrogen, oxygen, and sulfur donors in a noncoordinating and nonpolar solvent, cyclohexane. These solvation-minimized enthalpies[11] for the ZnTPP adducts allow us to incorporate this acid into the E and C correlation[13,14] and compare this acid quantitatively with other acids.

Experimental Section

Tetraphenylporphine and zinc tetraphenylporphine were synthesized by literature methods.[15,16] The ZnTPP was purified by dry-column chromatography.[10,16] Eastman tetrahydrothiophene (THTP) was refluxed over calcium hydride for 3 h and distilled from lithium aluminum hydride. Fisher Spectranalyzed pyridine was dried over barium oxide for 2 days and then distilled from fresh barium oxide at a pressure of 145 Torr (bp 65 °C). Chemicals Procurement Laboratories, Inc., 7-oxabicyclo[2.2.1]heptane (bridge ether) was stored over calcium hydride for 1 day and then distilled from fresh calcium hydride. Fisher Spectranalyzed dimethyl sulfoxide (Me_2SO) was dried over Linde 4A molecular sieves for 1 week and then distilled from calcium hydride at 30 Torr (bp 67 °C). Care must be taken during distillation due to vigorous bumping of Me_2SO. Fisher Spectranalyzed cyclohexane was stored over Linde 4A molecular sieves as were the purified bases.

Due to the limited solubility of ZnTPP in cyclohexane, the concentration of ZnTPP was initially determined using a Perkin-Elmer