manganese centers calculated in this work is 2 ± 1 kbar. Finally, the small change of the emission energy as a function of pressure strongly argues against a mechanism involving thermal population of excited states under high pressure. An internal pressure of the order of several hundred kilobar would be required in order for the ground and ^4E excited states to be separated by an energy of the order of kT at room temperature.

Acknowledgment. J.I.Z. gratefully acknowledges the Army Research Office (Durham) for the support of this work, the Alexander von Humboldt Society for a fellowship at the Universität Regensburg, and the Camille and Henry Dreyfus Teacher-Scholar Award.

Registry No. $((CH_3)_3NH)_3Mn_2Cl_7$, 58150-41-7; $(CH_3)_4NMnCl_3$, 31826-81-0.

Contribution from the Department of Chemistry,
University of California, Riverside, California 92521

Electrochemical and Spectroscopic Studies of Tris(3,5-di-*tert*-butylcatecholato)manganese(IV) and Its Dioxygen Adduct

KEITH D. MAGERS, CECIL G. SMITH, and DONALD T. SAWYER*

Received May 14, 1979

Tris(3,5-di-*tert*-butylcatechol) anion (DTBC) complexes of manganese(II), -(III), and -(IV) have been studied in aprotic solvents by electrochemical, spectroscopic, and magnetic methods. The blue $[Mn^{IV}(DTBC^{2-})_3]^{2-}$ complex reversibly binds oxygen at room temperature to form a red-brown complex $[Mn^{IV}(DTBC^{2-})_2(SQ^{-}\cdot)(O_2^{-}\cdot)]^{2-}$ (SQ = semiquinone) with an apparent formation constant of 2.9 atm^{-1} at 25 °C.

Manganese is an essential element in a number of biological systems.[1] In two of these, photosystem II in green plant photosynthesis[2-5] and certain superoxide dismutases,[6] manganese appears to serve as an electron-transfer agent in reactions that involve molecular oxygen and its reduced states. This has prompted interest in the interactions of molecular oxygen with manganese(II), -(III), and -(IV) complexes which may serve as biological model systems. The manganese complexes that are formed by polyhydroxy ligands are attractive model systems because of their ability to stabilize and solubilize the +3 and +4 oxidation states and to resist irreversible oxidation.[7-11] Several of these complexes react reversibly with molecular oxygen and peroxide ion.[7-9,11]

Although several manganese–catechol complexes have been reported,[12-20] most of the studies have been concerned with the comparison of metal–catechol formation constants[14,16,17,20] and metal-catalyzed autoxidations of catechol.[15,18] The aqueous chemistry of tris(catecholato) complexes of manganese(II) and -(III) has been described as well as the reversible oxidation of tris(3,5-di-*tert*-butylcatecholato)manganese(III) ($[Mn^{III}(DTBC)_3]^{3-}$) to form a unique tris(semiquinonato)-manganese(III) complex.[10] A recent communication[21] has reported that the oxidation product of $Mn^{III}(DTBC)_3{}^{3-}$ reversibly binds molecular oxygen in dimethyl sulfoxide at room temperature.

The present paper summarizes the electrochemical, spectroscopic, and magnetic characterization of the oxygen-binding species $Mn^{IV}(DTBC)_3{}^{2-}$ and its O_2 adduct in aprotic solvents. Related studies of the DTBC complexes of manganese(II) and -(III) also are discussed. The $Mn^{IV}(DTBC)_3{}^{2-}$ complex appears to be the first example of a reversible oxygen-binding metal center that is complexed by catecholate ligands.[22-26] The only other example is the $V^{IV}(DTBC)_2$ complex,[27,28] which binds oxygen with a 1:2 O_2:metal ratio.

Experimental Section

Equipment. Cyclic voltammetry measurements were made with a three-electrode potentiostat based on the use of solid-state operational amplifiers.[29] A Princeton Applied Research Model 173 Potentiostat/Galvanostat with the Model 175 universal programmer and Model 179 digital coulometer also was used for cyclic voltammetry and controlled potential electrolysis. Cyclic voltammograms were recorded on Houston Instrument Series 2000 and Hewlett-Packard Model 7030A X-Y recorders.

The Leeds and Northrup electrochemical cell has been described by Sawyer and Roberts[30] and was equipped with a Beckman platinum-inlay working electrode (area 0.23 cm^2), a platinum-flag auxiliary

---

(1) G. L. Lawrence and D. T. Sawyer, *Coord. Chem. Rev.*, **27**, 173 (1978).
(2) R. L. Heath, *Int. Rev. Cytol.*, **34**, 49 (1973).
(3) R. E. Blankenship, Ph.D. Dissertation, University of California, Berkeley, Calif., 1974.
(4) R. Radmer and G. M. Cheniae in "Primary Processes", in press.
(5) A. J. Bearden and R. Malkin, *Q. Rev. Biophys.*, **7**, 131 (1975).
(6) A. M. Michelson, J. M. McCord, and I. Fridovich, Eds., "Superoxide and Superoxide Dismutases", Academic Press, New York, 1977.
(7) M. E. Bodini, L. A. Willis, T. L. Riechel, and D. T. Sawyer, *Inorg. Chem.*, **15**, 1538 (1976).
(8) M. E. Bodini and D. T. Sawyer, *J. Am. Chem. Soc.*, **98**, 8366 (1976).
(9) D. T. Sawyer, M. E. Bodini, L. A. Willis, T. L. Riechel, and K. D. Magers, *Adv. Chem. Ser.*, **No. 162**, 330–49 (1977).
(10) K. D. Magers, C. G. Smith, and D. T. Sawyer, *Inorg. Chem.*, **17**, 515 (1978).
(11) D. T. Richens, C. G. Smith, and D. T. Sawyer, *Inorg. Chem.*, **18**, 706 (1979).
(12) R. Weinland and H. Sperl, *Z. Anorg. Allg. Chem.*, **150**, 69 (1925).
(13) J. Dolezal and J. Adam, *Collect. Czech. Chem. Commun.*, **20**, 985 (1955).
(14) Y. Murakami, K. Nakamura, and M. Tokunaga, *Bull. Chem. Soc. Jpn.*, **36**, 669 (1963).
(15) R. R. Grinstead, *Biochemistry*, **3**, 1308 (1964).
(16) R. F. Jameson and W. F. S. Neillie, *J. Inorg. Nucl. Chem.*, **28**, 2667 (1966).
(17) C. A. Tyson and A. E. Martell, *J. Am. Chem. Soc.*, **90**, 3379 (1968).
(18) C. A. Tyson and A. E. Martell, *J. Am. Chem. Soc.*, **94**, 939 (1972).
(19) E. Mentasti, E. Pelizzetti, E. Pramaurd, and G. Girandi, *Inorg. Chem. Acta*, **12**, 61 (1975).
(20) J. P. Scharff and R. Genin, *Anal. Chim. Acta*, **78**, 201 (1975).
(21) K. D. Magers, C. G. Smith, and D. T. Sawyer, *J. Am. Chem. Soc.*, **100**, 989 (1978).
(22) J. S. Valentine, *Chem. Rev.*, **73**, 235 (1973).
(23) L. Klevan, J. Peone, Jr., and S. K. Madan, *J. Chem. Educ.*, **50**, 670 (1973).
(24) F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, **8**, 384 (1975).
(25) L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976).
(26) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).
(27) J. P. Wilshire and D. T. Sawyer, *J. Am. Chem. Soc.*, **100**, 3972 (1978).
(28) J. P. Wilshire and D. T. Sawyer, unpublished results.
(29) A. D. Goolsby and D. T. Sawyer, *Anal. Chem.*, **39**, 411 (1967).
(30) D. T. Sawyer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists", Wiley-Interscience, New York, 1974, pp 144–5.

0020-1669/80/1319-0492$01.00/0

electrode, and an Ag/AgCl reference electrode filled with an aqueous tetramethylammonium chloride solution and adjusted to 0.000 V vs SCE. For controlled-potential electrolysis, a platinum-mesh working electrode and auxiliary electrode were employed.

Cary Model 14, Model 17D, and Model 219 spectrophotometers were used for UV–visible spectrophotometric measurements. Infrared spectra were obtained with a Perkin-Elmer Model 283 IR spectrophotometer by use of Nujol mulls and with matched NaCl and BaF_2 solution cells. Raman spectra were obtained with a Spex Raman spectrophotometer that was equipped with a 5-W argon laser. A rotating cell was used to retard the photodecomposition of the samples. ESR data were obtained with a Varian Model V-4500 spectrophotometer and a Varian Model E-3 spectrophotometer equipped with a liquid helium Dewar for low-temperature measurements. Flat and round quartz cells were used. Identical round cells positioned in the same manner were used for the spectra at liquid-helium temperatures. Magnetic susceptibility measurements were made with a Varian EM-390 NMR spectrophotometer.

Air-sensitive compounds were prepared in a Vacuum Atmospheres Corp. He-193-1 nitrogen-atmosphere glovebox. Many electrochemical measurements also were made in the glovebox.

Reagents. The reagents for the investigations and syntheses included: $Mn^{II}(ClO_4)_2$ (G. Frederick Smith), manganese(II) acetate (Alfa), 3,5-di-*tert*-butylcatechol ($DTBCH_2$) (Aldrich), 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) (Aldrich), tetraethylammonium hydroxide (25% in methanol, TEAOH) (Eastman), tetramethylammonium hydroxide (TMAOH) (MCB), sodium hydroxide (Mallinckrodt), dimethyl sulfoxide (Me_2SO) (Burdick and Jackson), dimethylformamide (DMF) (Burdick and Jackson), dimethylacetamide (DMA) (Burdick and Jackson), acetonitrile (AN) (Burdick and Jackson), propylene carbonate (Burdick and Jackson), pyridine (Burdick and Jackson), sodium perchlorate (G. Frederick Smith), and tetraethylammonium perchlorate (TEAP) (G. Frederick Smith).

The $Mn^{II}(DTBC)_3{}^{4-}$ complex was prepared in situ by adding $Mn^{II}(ClO_4)_2$, $DTBCH_2$, and tetraethylammonium hydroxide (TEAOH) in a mole ratio of 1:3:6 to dearated solvent. An attempt was made to isolate this complex as a solid from an oxygen-free DMF solution in which 0.1 M $Mn^{II}(ClO_4)_2$, 0.3 M $DTBCH_2$, and 0.6 M TEAOH were combined. The solvent was evaporated until a white precipitate appeared. The collected product was extremely oxygen sensitive, slowly oxidizing to a red product in a nitrogen glovebox with an O_2 content of less than 1 ppm. After recrystallization from acetonitrile, the product was dried and analyzed. The product appeared to consist of a mixture of bis- and tris(3,5-di-*tert*-butylcatecholato)manganese(II).[31]

The $Mn^{III}(DTBC)_3{}^{3-}$ complex was prepared in situ by combining $Mn^{II}(ClO_4)_2$, $DTBCH_2$, TEAOH, and 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ)[32] in a ratio of 2:5:10:1 to a deaerated solution. The manganese(III) complex also could be prepared in the same manner as the Mn(II) complex by use of $Mn^{III}(OAc)_3$[33] in place of $Mn^{II}(ClO_4)_2$. A $Mn^{III}(DTBC)_3{}^{3-}$ salt was obtained in an oxygen-free Me_2SO solution by combining 0.1 M $Mn^{II}(ClO_4)_2$, 0.25 M $DTBCH_2$, 0.5 M TEAOH, and 0.05 M DTBQ. The solution was evaporated until a red precipitate appeared. This solid also was oxygen sensitive (exposure to O_2 resulted in a blue product species). Elemental analysis of the dried red-brown precipitate gave results which were consistent with the formula $(TEA)_3[Mn^{III}(DTBC)_3]$. Anal. Calcd for $C_{66}H_{120}N_3O_6Mn_1$: C, 71.67; H, 10.86; N, 3.80; Mn, 4.98. Found: C, 68.71; H, 10.33; N, 3.77; Mn, 4.70 (Galbraith Laboratories, Inc.).

The $Mn^{IV}(DTBC)_3$ complex was prepared in situ by the combination of $Mn^{II}(ClO_4)_2$, $DTBCH_2$, TEAOH, and DTBQ in a ratio of 1:2:4:1 to a degassed solution. This complex also was prepared by oxidation of the Mn(III) complex with molecular oxygen. Attempts were made to isolate a salt of this complex from deaerated acetonitrile solution by combining 0.1 M $Mn^{II}(ClO_4)_2$, 0.2 M $DTBCH_2$, 0.4 M TEAOH, and 0.1 M DTBQ. Most of the acetonitrile was evaporated to yield an oil which was then recrystallized from acetonitrile to give a blue powder. This powder was extremely soluble in acetonitrile and yielded a blue solution which reversibly bound molecular oxygen. A sodium salt of the complex was obtained by mixing an acetonitrile solution (saturated with $NaClO_4$) with an equal volume of a solution that contained $(TEA)_2[Mn^{IV}(cat)_3]$. In the original synthesis, either NaOH or tetramethylammonium hydroxide was used in place of TEAOH. Because of the limited solubility of these two bases in acetonitrile, the solution had to be mixed approximately 24 h before the synthesis reaction was initiated. Elemental analysis on the sodium and tetramethylammonium salt was consistent with the formulation $[Mn^{IV}(DTBC)_3]^{2-}$ but also indicated an excess of sodium and tetramethylammonium cations, probably as precipitated perchlorate salts.

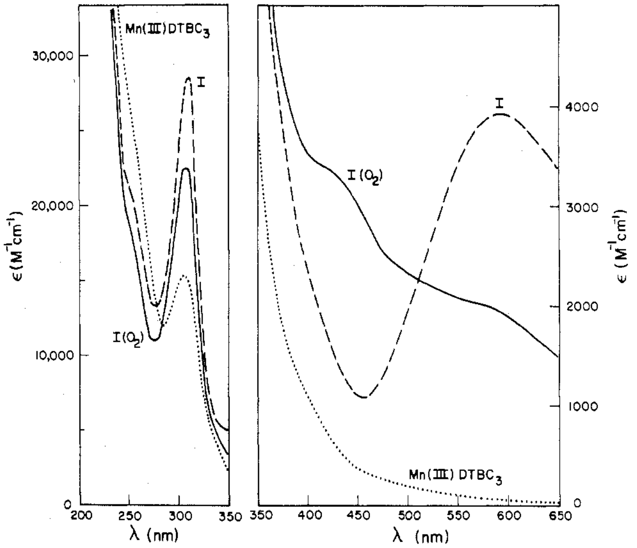

Figure 1. UV–visible absorption spectra for 1 mM solutions of $[Mn^{III}(DTBC^{2-})_3]^{3-}$, $[Mn^{IV}(DTBC^{2-})_3]^{2-}$ (I), and $[Mn^{IV}(DTBC^{2-})_2(SQ^{-}\cdot)(O_2{}^{-}\cdot)]^{2-}$ ($I(O_2)$) in acetonitrile.

The oxygen adduct of $Mn^{IV}(DTBC)_3{}^{2-}$ was prepared by bubbling molecular oxygen through the solution for 5–10 min. For the equilibrium studies, oxygen mixtures of 100% v/v (high-purity O_2), 21% (air passed through anhydrous $CaSO_4$ and Ascarite to remove impurities), 4.94% (Matheson), and 1.98% (liquid carbonic) were used. These studies were carried out at room temperature (298 K) and in a CCl_4 slush (251.5 K). Deoxygenation of the complex was accomplished by bubbling purified argon through the solution. Isolation of a pure solid product of the oxygen adduct proved to be impossible because of the enhanced rate of decomposition with increased concentration.

Magnetic susceptibility measurements were by the method of Evans[34] as modified by Rettig[35] and made use of the paramagnetic shift of the methyl protons of the acetonitrile solvent. Diamagnetic corrections were made.[36]

Results

Optical Spectroscopy. The tris(3,5-di-*tert*-butylcatecholato)manganese(II) complex, which is colorless when prepared in the total absence of oxygen, reacts with trace amounts of oxygen to form the yellow-brown tris(3,5-di-*tert*-butylcatecholato)manganese(III) complex. In acetonitrile, the spectrum of the manganese(III) complex (Figure 1) exhibits a weak shoulder at about 500 nm, which corresponds to a d–d electronic transition, and an intense band at 305 nm, which corresponds to a ligand π–π^* transition similar to those observed with other metal catechol complexes.[17,27,28,37–42]

---

(31) Recrystallization from acetonitrile may have favored the formation of the dinegative $[Mn^{II}(DTBC)_2]^{2-}$ complex over the tetranegative $[Mn^{II}(DTBC)_3]^{4-}$ complex.

(32) DTBQ must be added last in all of the preparations.

(33) G. Breuer, "Handbook of Preparative Inorganic Chemistry", Vol. 2, 2nd ed., Academic Press, New York, 1965, p 1469.

(34) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(35) M. F. Rettig, private communication, University of California, Riverside.

(36) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins, Eds., Interscience, New York, 1960.

(37) L. Havelkova and M. Bartusek, *Collect. Czech. Chem. Commun.*, **34**, 2919 (1969).

(38) J. L. Martin and J. Takats, *Can. J. Chem.*, **53**, 572 (1975).

(39) P. A. Wickland and D. G. Brown, *Inorg. Chem.*, **15**, 396 (1976).

(40) D. G. Brown, *Inorg. Nucl. Chem. Lett.*, **12**, 399 (1976).

Spectroscopic mole ratio studies indicate that the ligand-to-metal stoichiometry for this complex is 3:1. Oxygenation of this complex appears to first produce the blue manganese(IV) catechol complex and then the red-brown dioxygen adduct (Figure 1).

Spectroscopic results indicate that the optimal base:ligand:metal ratio for the formation of the intensely blue complex is 6:3:1, which is consistent with the formulation $[\mathrm{Mn^{IV}(DTBC)_3}]^{2-}$.[43] This manganese(IV) complex, I, exhibits a ligand-to-metal charge-transfer band at 590 nm and an enhanced π–π^* band at 300 nm. Oxygenation of this complex yields a red-brown oxygen adduct, $\mathrm{I(O_2)}$, with a distinguishing band at 450 nm and a π–π^* transition at 300 nm (Figure 1). The formation of the oxygen adduct is reversible at room temperature and yields closely similar spectra for I and for $\mathrm{I(O_2)}$ after several deoxygenation–oxygenation cycles (the respective absorbances decrease less than 5% per cycle). The adduct undergoes a slow, irreversible oxidation to form first a green and then a yellow solution.[44] The dioxygen adduct rapidly oxidizes when exposed to air unless that air has been passed through anhydrous calcium sulfate and Ascarite. Oxygenation and deoxygenation of the complex are rapid and occur within the few minutes necessary to saturate the solution with oxygen and argon, respectively. Similar results are obtained for I and $\mathrm{I(O_2)}$ in $\mathrm{Me_2SO}$, DMF, and DMA, but the reversibility is optimal in acetonitrile. The extent of oxygen binding in propylene carbonate and pyridine is low. As the concentration of the complex is increased, the formation of the oxygen adduct becomes inhibited.

The formation constant, K_f, for the oxyygen adduct has been determined spectrophotometrically by monitoring the absorbance at 450 nm for different partial pressures of oxygen (P_{O_2}). The results are consistent with the relation[45]

$$\log \frac{A - A_0}{A_\infty - A} = \log \frac{[\mathrm{I(O_2)}]}{[\mathrm{I}]} = n \log P_{O_2} + \log K_f \quad (1)$$

which represents the binding of n oxygen molecules per complex molecule. Plots of log $([\mathrm{I(O_2)}]/[\mathrm{I}])$ vs. log P_{O_2} yield straight lines with an average slope of 0.8 which is indicative of a one-to-one oxygen adduct. The apparent formation constant is 2.9 atm^{-1} at 298 K and 3.2 atm^{-1} at 251.5 K.[46]

Vibrational Spectroscopy. The isolated tetraethylammonium salt of the $\mathrm{(DTBC)_3}$ complex of manganese(III) has IR bands (1550 (m), 1416 (s), 1279 (s), 1237 (s), 1201 (m), 979 (s) cm^{-1}) that are consistent with those reported for bound catechol.[39,40,47–54] The tetramethylammonium and sodium salts of the corresponding manganese(IV) complex have similar IR spectra (1545 (m), 1414 (s), 1282 (s), 1240 (s), 1207 (m), 983 (s) cm^{-1}; 1548 (m), 1411 (s), 1282 (s), 1237 (s), 1204 (m), 980 (s) cm^{-1}, respectively). The absence of a C=O stretching band in the region of 1700 cm^{-1} confirms that these complexes do not contain the *o*-quinone. A similar absence of OH stretching bands indicates that the catechol ligands are fully deprotonated and that aquo or hydroxo ligands are not bound to the manganese. The IR spectra also indicate the absence of any acetonitrile in these complexes.

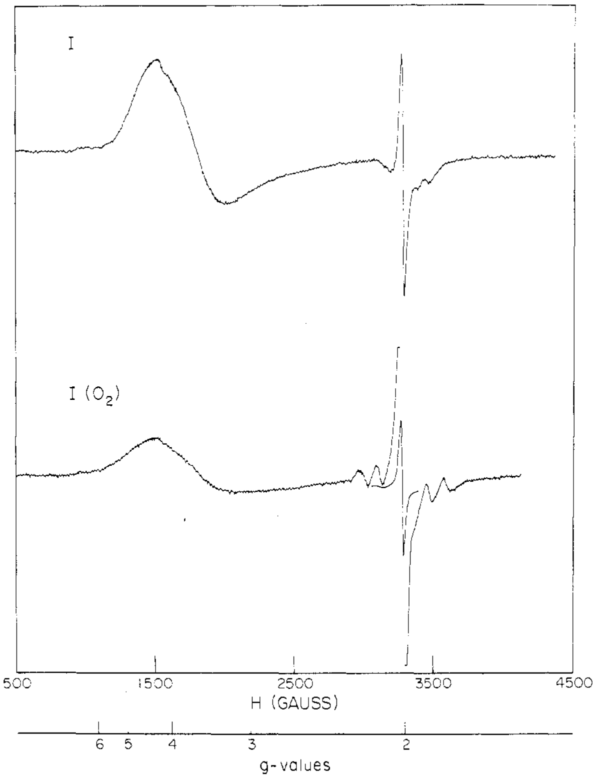

Figure 2. ESR spectra for 1 mM solutions of $[\mathrm{Mn^{IV}(DTBC^{2-})_3}]^{2-}$ (I) and $[\mathrm{Mn^{IV}(DTBC^{2-})_2(SQ^{-}\cdot)(O_2^{-}\cdot)}]^{2-}$ ($\mathrm{I(O_2)}$) in frozen acetonitrile at 4.2 K. Spectrometer settings: microwave frequency, 9.252 GHz; microwave power, 0.5 mW; modulation amplitude, 10 G; signal level, 1×10^4 (signal level is reduced to 1×10^3 for the large $g \simeq 2$ signal for $\mathrm{I(O_2)}$).

Useful infrared spectra of the oxygen adduct in acetonitrile are difficult to obtain because of interfering solvent bands and the necessity that low concentrations of complex be used to minimize chemical degradation. Assignment of an O–O stretching band in either the "superoxo" (1075–1195 cm^{-1}) or the "peroxo" (790–932 cm^{-1}) region of the IR spectrum[55] has not been possible. The IR spectra indicate that some *o*-quinone of DTBC is formed after oxygenation and disappears after oxygen removal.

Useful Raman spectra of the oxygen carrier in acetonitrile also have been difficult to obtain because of solvent interference, high background fluorescence, decomposition of sample in the laser beam, and the necessity to use low concentrations of complex. Even attempts to make use of the resonance Raman effect have failed to yield reliable data for the O–O stretching bands of the adduct.

Magnetic Measurements. A 10 mM solution of I in acetonitrile has a magnetic moment of 3.94 μ_B, which is indicative of a high-spin (d^3) manganese(IV) complex. With oxygenation, the magnetic moment decreases to 2.61 μ_B. Because

---

(41) J. P. Wilshire, L. Leon, P. M. Bosserman, and D. T. Sawyer, *J. Am. Chem. Soc.*, **101**, 3379 (1979).

(42) J. P. Wilshire, L. Leon, P. M. Bosserman, D. T. Sawyer, R. M. Buchanan, and C. G. Pierpont, "Third Internation Conference on the Chemistry and Uses of Molybdenum", H. F. Barry and P. C. H. Mitchell, Eds., Climax Molybdenum Co., Ann Arbor, Mich., in press.

(43) The complex may also be formulated $[\mathrm{Mn^{III}(DTBC)_2(SQ^{-}\cdot)}]^{2-}$ where $\mathrm{SQ^{-}\cdot}$ represents the semiquinone radical of DTBC.

(44) This reaction requires several hours at room temperature.

(45) A_∞ represents the absorbance for pure $\mathrm{I(O_2)}$, A_0 is for pure I, and A is the measured absorbance for the equilibrium mixture of $\mathrm{I(O_2)}$ and I.

(46) Because formation of the oxygen adduct does not approach completion at an oxygen partial pressure of 1 atm, the value for A_∞ in eq 1 had to be estimated by successive approximations. The poor reproducibility of the spectroscopic measurements for the $\mathrm{O_2}$ complex limited the precision of the values for the equilibrium constants.

(47) C. MacDonald, A. J. Tomlinson, and C. J. Willis, *Can. J. Chem.*, 2578 (1971).

(48) D. C. Patel and P. K. Bhattachrya, *J. Inorg. Nucl. Chem.*, **33**, 529 (1971).

(49) R. P. Henry, P. C. H. Mitchell, and J. E. Prue, *J. Chem. Soc., A*, 3392 (1971).

(50) A. L. Balch and Y. S. Sohn, *J. Organomet. Chem.*, **30**, C31 (1971).

(51) Y. S. Sohn and A. L. Balch, *J. Am. Chem. Soc.*, **94**, 1144 (1972).

(52) L. G. Abakumova, G. A. Domrachev, and G. A. Abakumov, *Zh. Obshch. Khim.*, **44**, 823 (1974).

(53) A. Y. Giris, Y. S. Sohn, and A. L. Balch, *Inorg. Chem.*, **14**, 2328 (1975).

(54) M. Ghedini, G. Dolcetti, B. Giovannitti, and G. Denti, *Inorg. Chem.*, **16**, 1725 (1977).

(55) L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976).

$I(O_2)$ is not completely formed under these conditions, the decrease only provides qualitative evidence for spin-pairing with adduct formation. When the bound oxygen is removed to regenerate I, the magnetic moment returns to 3.95 μ_B and further confirms the reversibility of the oxygenation process.

ESR Spectroscopy. Figure 2 illustrates the ESR spectrum of I in frozen acetonitrile at 4.2 K, with a $g_\perp$ value of 3.67 and a $g_\parallel$ value of about 2. The spectrum is consistent with that for a $S = {}^3/_2$ system in an axial field with a large zero-field splitting.[56-62] Such a pattern provides additional support for the formulation of I as a tris(catecholato)manganese(IV) complex. The sharp resonance at $g = 2$ indicates that small amounts of free semiquinone anion radical apparently are in equilibrium with the complex. At room temperature, only the characteristic multiline spectrum of the free semiquinone[63,64] is observed.

The ESR spectrum for a frozen acetonitrile solution of $I(O_2)$ at 4.2 K also is illustrated in Figure 2. Oxygenation significantly decreases the ESR signal for I but does not eliminate it because I remains in equilibrium with $I(O_2)$ under these conditions. The signal due to semiquinone radical increases significantly, which indicates that the mechanism by which molecular oxygen is bound involves the oxidation of catechol ligand to either free or bound semiquinone. A hyperfine splitting which is partially obscured by the radical signal also occurs in the region of $g = 2$. This signal appears to have six lines and a large splitting constant ($A_{Mn} \simeq 130$ G) that is characteristic of manganese hyperfine splitting. As expected, the $(DTBC)_3Mn^{III}$ complex is ESR silent.

Electrochemistry. The cyclic voltammetry of the $(DTBC)_3$ complex of manganese(III) in Me_2SO is illustrated by Figure 3a.[65] The initial cathodic peak at −1.75 V vs. SCE is coupled to the anodic peak at −0.75 V. The electrochemistry of the Mn(II)–DTBC complex includes an initial oxidation peak at −0.75 V and a corresponding reduction at −1.75 V. Controlled-potential electrolysis confirms that the oxidation of the manganese(II) complex at −0.75 V is a one-electron process that yields the brown-yellow manganese(III) complex. Controlled-potential electrolysis has not been effective for the determination of the electron stoichiometry of the reduction at −1.75 V because of the proximity of the solvent reduction potential. However, the electrolysis does change the manganese(III) solution to a colorless solution that is characteristic of the manganese(II) complex.

The initial anodic peak at −0.45 V of Figure 3a corresponds to a one-electron oxidation of the manganese(III) complex. Controlled-potential electrolysis at this potential produces the intense blue color characteristic of the manganese(IV) complex. The oxidation peak at −0.27 V apparently is due to the one-electron oxidation of catechol ligand; a reduction corresponding to this oxidation occurs at −0.50 V. The oxidation peak at +0.10 V corresponds to a multielectron process in which the ligands are further oxidized. Controlled-potential electrolysis indicates that the product of this oxidation is the free quinone (DTBQ). This oxidation peak is coupled to a multistep reduction peak at −0.37 V.

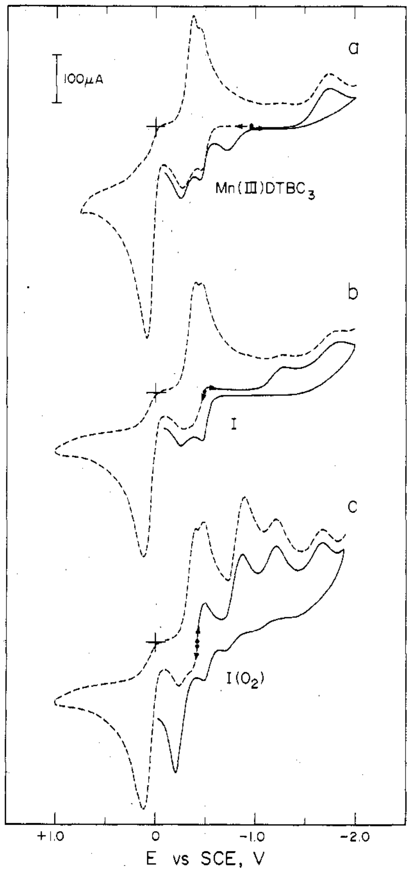

Figure 3. Cyclic voltammograms for 5 mM solutions of (a) $[Mn^{III}(DTBC^{2-})_3]^{3-}$, (b) $[Mn^{IV}(DTBC^{2-})_3]^{2-}$ (I), and (c) $[Mn^{IV}(DTBC^{2-})_2(SQ^{-}\cdot)(O_2^{-}\cdot)]^{2-}$ ($I(O_2)$) in Me_2SO which contains 0.1 M tetraethylammonium perchlorate. Scan rate is 0.1 V/s. All scans originate at the rest potential for the solution.

The $(DTBC)_3Mn^{IV}$ complex exhibits the electrochemistry illustrated by Figure 3b.[65] A small initial cathodic peak at −0.50 V is followed by reductions at −1.30 V and −1.85 V, which yield a product that does not exhibit an oxidation at −0.75 V but does undergo an oxidation at −0.45 V. This indicates that the reduction product is $(DTBC)_3Mn^{III}$ and that the two peaks (−1.30 and −1.85 V) are due to a two-step one-electron reduction. The broad peak at −0.30 V for an initial positive scan of the $(DTBC)_3Mn^{IV}$ complex probably is due to superimposed peaks for the oxidation of a catechol ligand to bound semiquinone anion and the oxidation of free ligand in equilibrium with the complex.[66] This anodic peak is coupled to a cathodic peak at −0.48 V.

The oxygen adduct $[I(O_2)]$ exhibits an initial cathodic peak at −0.50 V, which appears to be a one-electron process (Figure 3c). The appearance of this peak indicates that oxygen oxidizes ligand and binds to the metal in a reduced state. The peak at −0.90 V corresponds to the reduction of free molecular oxygen to superoxide ion, while the two peaks at −1.20 and −1.68 V correspond to the reduction of manganese(IV) itself. The reverse positive scan yields a large peak at −0.21 V due to displaced catechol monoanion. The initial positive scan for $[I(O_2)]$ yields partially superimposed oxidation peaks at −0.30 V. These peaks probably correspond to the oxidation of the bound catechol of I (that fraction that is not bound to O_2) and to the oxidation of free ligand.[66] The unique electrochemical

---

(56) L. S. Singer, *J. Chem. Phys.*, **23**, 379 (1955).
(57) T. M. Lambe, J. C. Tobin, and F. L. Scott, *Chem. Commun.*, 411 (1971).
(58) S. Laniry and V. K. Anand, *Chem. Commun.*, 1111 (1971).
(59) S. A. Cotton and J. F. Gibson, *J. Chem. Soc. A*, 803 (1971).
(60) M. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 533 (1972).
(61) D. C. Bradley, R. G. Copperthwaite, S. A. Cotton, K. D. Sales, and J. F. Gibson, *J. Chem. Soc., Dalton Trans.*, 191 (1973).
(62) D. T. Richens and D. T. Sawyer, *J. Am. Chem. Soc.*, **101**, 3681 (1979).
(63) O. Ryba, J. Pilar, and J. Petranek, *Collect. Czech. Chem. Commun.*, **33**, 26 (1968).
(64) C. Trapp, C. A. Tyson, and G. Giacometti, *J. Am. Chem. Soc.*, **90**, 1394 (1968).
(65) In Figure 3, the cyclic voltammograms do not exhibit significant peaks at the −0.24 oxidation potential for free catechol monoanion. This indicates that most of the catechol is bound to form tris complexes.
(66) The manganese(IV) complex probably is in equilibrium with catechol monoanion, semiquinone anion, quinone and manganese(III) complexes.

features of I and $I(O_2)$ are reproducible during the course of several oxygenation cycles.

The electrochemistry for the Mn–DTBC complexes is similar in other aprotic solvents. In acetonitrile, however, adsorption effects result in poorly defined cyclic voltammograms.

Discussion. The results presented in this paper indicate that DTBC forms stable manganese(II), -(III), and -(IV) complexes. The manganese(IV) complex is especially significant because it can reversibly bind oxygen at room temperature.

From the electrochemical and spectroscopic data, the manganese(II) complex is oxidized by a one-electron process (eq 2). The corresponding reduction reaction (eq 3) is irreversible.

$$\underset{\mathrm{II}}{[\mathrm{Mn^{II}(DTBC^{2-})_3}]^{4-}} \xrightarrow{-0.75\ \mathrm{V}} \underset{\mathrm{III}}{[\mathrm{Mn^{III}(DTBC^{2-})_3}]^{3-}} + e^- \qquad (2)$$

$$\mathrm{III} + e^- \xrightarrow{-1.75\ \mathrm{V}} \mathrm{II} \qquad (3)$$

The manganese(III) complex undergoes an apparent one-electron oxidation to form a product which, on the basis of ESR and magnetic susceptibility measurements, has three unpaired electrons. This is consistent with the formation of high-spin manganese(IV) (eq 4).

$$\mathrm{III} \xrightarrow{-0.45\ \mathrm{V}} \underset{\mathrm{I}}{[\mathrm{Mn^{IV}(DTBC^{2-})_3}]^{2-}} + e^- \qquad (4)$$

The reaction also may be expressed as an oxidation of a catechol ligand to semiquinone anion (eq 5) with spin pairing between an unpaired d electron and the unpaired electron of the radical to give a $S = {}^3/_2$ spin system.

$$\mathrm{III} \xrightarrow{-0.45\ \mathrm{V}} \underset{\mathrm{Ia}}{[\mathrm{Mn^{III}(DTBC^{2-})_2(SQ^{-}\cdot)}]^{2-}} + e^- \qquad (5)$$

The reduction of I appears to involve a two-step one-electron process to form III (eq 6).

$$\mathrm{I} + e^- \xrightarrow{-1.30\ \mathrm{V}} \mathrm{I{-}III} \xrightarrow{-1.85\ \mathrm{V}} \mathrm{III} \qquad (6)$$

The intermediate reduction product, I–III, may correspond to a manganese(III–IV) dimer.

The oxidation of I seems to be a one-electron process with oxidation of bound catechol to semiquinone (eq 7).

$$\mathrm{I} \xrightarrow{-0.3\ \mathrm{V}} \underset{\mathrm{IV}}{[\mathrm{Mn^{IV}(DTBC^{2-})_2(SQ^{-}\cdot)}]^{-}} + e^- \qquad (7)$$

Regeneration of I results from reduction (eq 8).

$$\mathrm{IV} + e^- \xrightarrow{-0.50\ \mathrm{V}} \mathrm{I} \qquad (8)$$

The overall reaction for the multistep oxidation of IV can be represented by eq 9.

$$\mathrm{IV} \xrightarrow{+0.10\ \mathrm{V}} \mathrm{Mn^{II}} + 3\mathrm{DTBQ} + 3e^- \qquad (9)$$

The quinone formed in this oxidation is a poor ligand which does not complex with manganese(IV). Without effective ligand stabilization, manganese(IV) is reduced to manganese(II) via oxidation of ligand. A reasonable mechanism for this reaction involves an initial oxidation of bound catechol to form a neutral complex which is susceptible to disproportionation and further oxidation reactions (eq 9a–d).

$$\mathrm{IV} \rightarrow \underset{\mathrm{V}}{[\mathrm{Mn^{IV}(DTBC^{2-})(SQ^{-}\cdot)_2}]^{0}} + e^- \qquad (9a)$$

$$\mathrm{V} \rightarrow \underset{\mathrm{(VI)}}{[\mathrm{Mn^{IV}(DTBC^{2-})(SQ^{-}\cdot)}]^{+}} + {}^1/_2\mathrm{DTBC^{2-}} + {}^1/_2\mathrm{DTBQ} \qquad (9b)$$

$$\mathrm{VI} \rightarrow \mathrm{Mn^{II}} + 2\mathrm{DTBQ} + e^- \qquad (9c)$$

$${}^1/_2\mathrm{DTBC^{2-}} \rightarrow {}^1/_2\mathrm{DTBQ} + e^- \qquad (9d)$$

The quinone (DTBQ) is reduced in the presence of manganese(II) to yield IV (eq 10).

$$3\mathrm{DTBQ} + \mathrm{Mn^{II}} + 3e^- \xrightarrow{-0.37\ \mathrm{V}} \mathrm{IV} \qquad (10)$$

Both electrochemical and ESR measurements indicate that the oxygenation of I results in the oxidation of bound catechol to semiquinone. A reaction scheme consistent with the results is

$$\mathrm{I} + \mathrm{O_2} \rightarrow [\mathrm{Mn^{IV}(DTBC^{2-})_2(SQ^{-}\cdot)(O_2^{-}\cdot)}]^{2-} \qquad (11)$$

Spin coupling between unpaired electrons on the radicals and the manganese may explain the lower magnetic moment observed for the oxygen adduct. Such a representation of $I(O_2)$ implies seven-coordinate manganese with three bidentate ligands and one monodentate ligand ($O_2^{-}\cdot$). However, the bound semiquinone may act as a monodentate ligand with the sixth coordination site occupied by superoxide ion. Another possibility is the dissociation of the bound semiquinone as oxygen is bound (eq 12).

$$\mathrm{I} + \mathrm{O_2} \rightarrow [\mathrm{Mn^{IV}(DTBC^{2-})_2(O_2^{-}\cdot)(solvent)}]^{-} + \mathrm{SQ^{-}\cdot} \qquad (12)$$

The only other reported manganese(IV) oxygen adducts are the (*meso*-tetraphenylporphinato)manganese(IV) complexes.[67,68] These complexes correspond to $S = {}^3/_2$ spin systems and are thought to involve peroxo binding to give a $\mathrm{Mn^{IV}O_2^{2-}}$ species. Several manganese–Schiff base complexes appear to bind oxygen, but the complexes have not been well characterized.[69-71]

The Mn(IV)–DTBC (I) complex represents an interesting new category of oxygen carriers in which electron transfer from catecholate ligand to molecular oxygen is necessary for binding. It also represents an important model system for the biological interaction of oxygen with manganese, especially in the terminal oxygen releasing step in photosystem II.[1,2-4] This type of complex also may prove useful as an activator for oxygenation reactions. Additional investigations of manganese complexes with derivatives of catechol are in progress. The goal is to perfect a system which mimics the biological role of manganese in photosystem II.

Acknowledgment. This work was supported by the U.S. Public Health Service—NIH under Grant No. GM-22761 and the U.S. Department of Agriculture Forest Service, Forest Products Laboratory, Madison, Wis., under Agreement No. 12-167. We wish to thank Professor H. B. Gray (California Institute of Technology) for the use of the liquid-helium ESR facility.

Registry No. I, 72268-94-1; $I(O_2)$, 72301-22-5; $I(TMA)_2$, 72275-16-2; $I(Na)_2$, 72275-17-3; II, 72268-95-2; $(TEA)_3III$, 72268-96-3.

---

(67) B. M. Hoffman, C. J. Weschler, and F. Basolo, *J. Am. Chem. Soc.*, **98**, 5473 (1976).

(68) R. D. Jones, D. A. Summerville, and F. Basolo, *J. Am. Chem. Soc.*, **100**, 4416 (1978).

(69) G. L. Johnson and W. D. Beveridge, *Inorg. Nucl. Chem. Lett.*, **3**, 323 (1967).

(70) J. D. Miller and F. D. Oliver, *J. Inorg. Nucl. Chem.*, **34**, 1873 (1972).

(71) B. Chiswell, *Inorg. Chim. Acta*, **23**, 77 (1977).