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Manganese(III)-Catecholate Coordination in the Bis(tetrabromocatecholato)(triphenylphosphine oxide)manganese(III) Anionic Dimer

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Bis(tetrabromocatecholato)(triphenylphosphine oxide)manganese(III) anion can be formed by treating Mn^{2+} with tetrabromo-1,2-benzoquinone, triphenylphosphine, and base. The potassium salt recrystallized from aqueous acetone forms the solvated crystals $K[Mn(Br_4C_6O_2)_2(OPPh_3)]\cdot H_2O\cdot (CH_3)_2CO$. Crystals form in the monoclinic space group $P2_1/n$ with four formula units in a unit cell of dimensions $a = 10.256$ (2) Å, $b = 26.434$ (3) Å, $c = 14.965$ (2) Å, and $\beta = 102.23$ (1)°. The structure was solved by direct methods and refined to $R = 0.059$ and $R_w = 0.060$ for 1877 observed, independent reflections. The coordination geometry about each Mn ion is distorted octahedral with catecholate ligands chelated to the metal ions in a planar arrangement and the phosphine oxide ligand bonded in an apical site. The sixth coordination site of the octahedron is occupied by the catecholate oxygen of an adjacent complex anion. The result is a dimeric structure with complex ions in a face-to-face arrangement. Potassium ions interact with catecholate oxygens, forming a polymeric crystal structure consisting of cation and anion pairs. The charge distribution between metal and the quinone ligands is discussed in relation to the neutral semiquinone complex $Mn(SQ)_2$ reported previously.

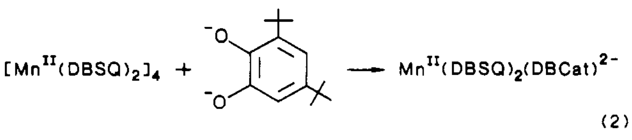
Introduction

Models proposed for the photosynthetic water oxidation system have included two pools of manganese ions, each containing two Mn atoms.[1] One pair of metal atoms associated with the hydrophobic "intrinsic" 34kD protein is thought to be directly involved with oxygen production. Electrons produced by the oxidation process have been proposed to be transferred from the water-oxidizing complex to a plastoquinone acceptor (Z), which, in turn, serves as an electron donor to the reaction center chlorophyll P680. Kambara and Govindjee have suggested that a redox-active ligand associated with the dimanganese center facilitates electron transfer from the metals to Z.[1a,b] This proposal, with identification of plastoquinone as the primary acceptor of charge from the water oxidation complex,[2] has stimulated study of manganese quinone complexes.[3,4] Quinone complexes provide examples of systems that contain redox-active ligands bonded to the metal ions, stabilize manganese ions in the high oxidation states associated with the water oxidation complex, and undergo reversible intramolecular electron transfer with the complexed manganese ion.[4]

In previous reports, the synthesis of the tetrameric semiquinone complex $[Mn(DBSQ)_2]_4$ (DBSQ = 3,5-di-*tert*-butylsemiquinonate) was described. The complex could be formed either by treating $Mn_2(CO)_{10}$ with 3,5-di-*tert*-butyl-1,2-benzoquinone or by treating Mn(II) with 3,5-di-*tert*-butylcatechol under oxidative conditions.[4] Upon treatment with pyridine (py) the monomeric adduct $Mn(py)_2(DBCat)_2$ (DBCat = 3,5-di-*tert*-butylcatecholate) is formed. With catecholate ligands chelated to Mn(IV), the charge distribution in the pyridine adduct is related to the $Mn(DBSQ)_2$ unit of the tetramer by transfer of two electrons between the quinone ligands and the metal ion. When conditions of solvent and temperature were varied, the equilibrium between Mn(II) and Mn(IV) forms of the complex could be studied (eq 1).[4] A Mn(III) form of the complex was not observed.

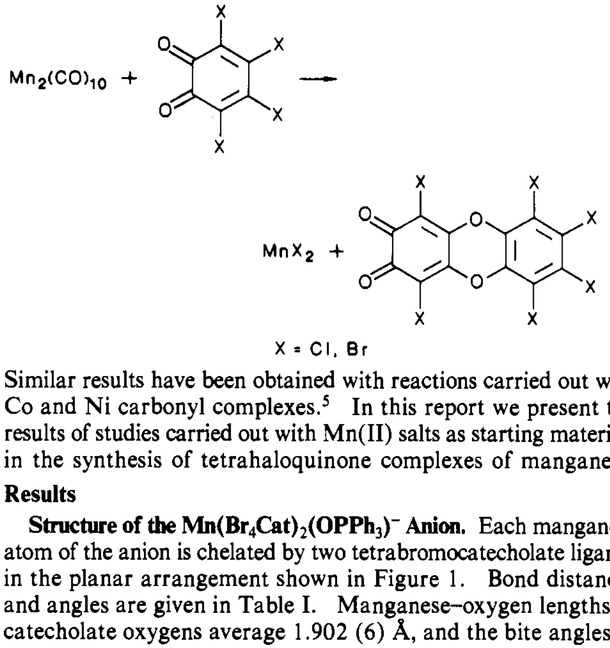
$$Mn^{II}(py)_2(DBSQ)_2 \rightleftarrows Mn^{IV}(py)_2(DBCat)_2 \qquad (1)$$

The tris(3,5-di-*tert*-butylcatecholato)manganese(IV) dianion, studied by Sawyer and Cooper,[3a,b] can be viewed as related to $Mn^{IV}(py)_2(DBCat)_2$ as a "catecholate adduct of $Mn(DBSQ)_2$" (eq 2) formed by addition, followed by intramolecular electron transfer. We have sought to extend this work to other quinone ligands and to include the tetrachloro- and tetrabromo-1,2-benzoquinones. Treatment of $Mn_2(CO)_{10}$ with the benzoquinone (eq 3) gave the manganese(II) dihalide and an organic product, which has been characterized as perchloro-2,3-oxanthrenequinone.



(2)

$$Mn^{II}(DBSQ)_2(DBCat)^{2-} \xrightarrow{ET} Mn^{IV}(DBCat)_3^{2-}$$



(3)

Similar results have been obtained with reactions carried out with Co and Ni carbonyl complexes.[5] In this report we present the results of studies carried out with Mn(II) salts as starting materials in the synthesis of tetrahaloquinone complexes of manganese.

Results

Structure of the $Mn(Br_4Cat)_2(OPPh_3)^-$ Anion. Each manganese atom of the anion is chelated by two tetrabromocatecholate ligands in the planar arrangement shown in Figure 1. Bond distances and angles are given in Table I. Manganese-oxygen lengths to catecholate oxygens average 1.902 (6) Å, and the bite angles at the metal average 85.5 (6)°. The Mn-O length is short for Mn(III), and the values found are quite similar to lengths and angles found for the two structure determinations on the Mn(IV)-catecholate complex $Mn(DBCat)_3^{2-}$ despite the difference in charge on the metal ion.[3a,b] Manganese-oxygen lengths ranging from 1.874 to 1.922 Å and ligand bite angles of 85.4° were

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(1) (a) Kambara, T.; Govindjee. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *88*, 6119-6123. (b) Govindjee; Kambara, T.; Coleman, W. *Photochem. Photobiol.* **1985**, *42*, 187-210. (c) Dismukes, G. C. *Photochem. Photobiol.* **1986**, *43*, 99-115. (d) Sauer, K. *Acc. Chem. Res.* **1980**, *13*, 249-256.

(2) Takahashi, Y.; Katoh, S. *Biochim. Biophys. Acta* **1986**, *848*, 183-192.

(3) (a) Chin, D.-H.; Sawyer, D. T.; Schaefer, W. P.; Simmons, C. J. *Inorg. Chem.* **1983**, *22*, 752-758. (b) Hartman, J. R.; Foxman, B. M.; Cooper, S. R. *Inorg. Chem.* **1984**, *23*, 1381-1387. (c) Mathur, P.; Dismukes, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 7093-7098. (d) Padhye, S. B.; Haltiwanger, R. C.; deLearie, L. A.; Pierpont, C. G., substituted for publication in *J. Chem. Soc., Chem. Commun.*

(4) (a) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1981**, *103*, 3961-3963. (b) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041-2049.

(5) Buchanan, R. M.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439-3444.

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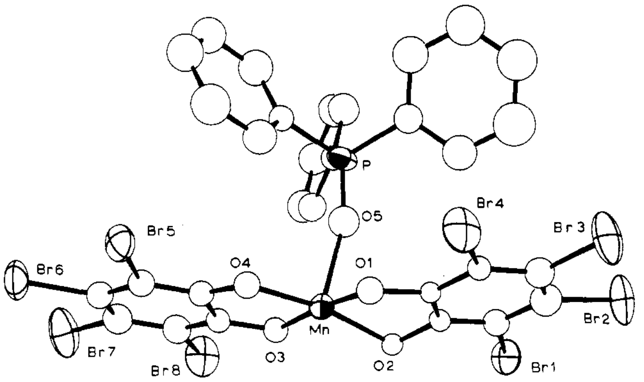

Figure 1. ORTEP plot showing the anionic $Mn(Br_4Cat)_2(OPPh_3)^-$ monomeric unit.

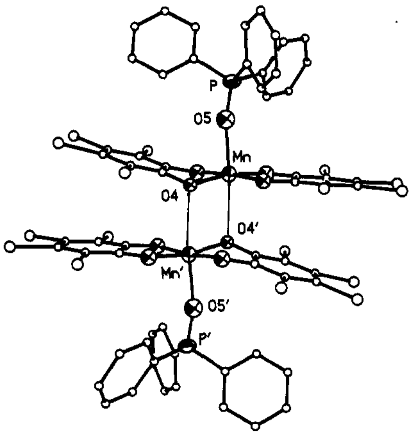

Figure 2. View of the weak dimeric interaction between $Mn(Br_4Cat)_2(OPPh_3)^-$ monomers. The Mn–O4′ length is 2.72 (1) Å, the Mn–O4′–Mn′ angle is 97.7 (2)°, and the Mn---Mn′ separation is 3.533 (6) Å.

Table I. Selected Bond Distances and Angles for $K[Mn(O_2C_6Br_4)_2(OPPh_3)]\cdot H_2O\cdot (CH_3)_2CO$

Interatomic Distances (Å)			
Mn–O1	1.913 (0.013)	Mn–O2	1.888 (0.013)
Mn–O3	1.897 (0.013)	Mn–O4	1.909 (0.012)
Mn–O5	2.135 (0.015)	Mn–O4′	2.723 (0.013)
Br1–C3	1.896 (0.021)	Mn–Mn′	3.533 (0.008)
Br2–C4	1.916 (0.022)	Br3–C5	1.879 (0.023)
Br4–C6	1.877 (0.022)	Br5–C9	1.900 (0.021)
Br6–C10	1.884 (0.025)	Br7–C11	1.860 (0.023)
Br8–C12	1.864 (0.020)	P–O5	1.492 (0.015)
P–C13	1.803 (0.012)	P–C19	1.805 (0.012)
P–C30	1.782 (0.019)	O1–C1	1.333 (0.022)
O2–C2	1.324 (0.022)	C1–C2	1.424 (0.026)
C1–C6	1.389 (0.027)	C2–C3	1.363 (0.026)
C3–C4	1.382 (0.027)	C4–C5	1.378 (0.027)
C5–C6	1.391 (0.028)	O3–C7	1.365 (0.021)
O4–C8	1.348 (0.021)	C7–C8	1.405 (0.024)
C7–C12	1.371 (0.025)	C8–C9	1.374 (0.026)
C9–C10	1.402 (0.029)	C10–C11	1.382 (0.029)
C11–C12	1.423 (0.027)	K–O1′	2.800 (0.015)
K–O3	2.845 (0.014)	K–O4′	2.855 (0.014)
K–O6	2.995 (0.016)	K–O6′	2.794 (0.015)
K–O7′	2.692 (0.016)		
Angles (deg)			
O2–Mn–O1	85.6 (0.6)	O3–Mn–O1	174.6 (0.6)
O3–Mn–O2	94.6 (0.6)	O4–Mn–O1	93.4 (0.6)
O4–Mn–O2	168.4 (0.6)	O4–Mn–O3	85.3 (0.6)
O5–Mn–O1	93.5 (0.6)	O5–Mn–O2	98.0 (0.6)
O5–Mn–O3	91.8 (0.6)	O5–Mn–O4	93.5 (0.6)
O6–K–O3	60.3 (0.4)	C13–P–O5	111.1 (0.9)
C19–P–O5	108.9 (0.8)	C19–P–C13	109.3 (0.7)
C30–P–O5	112.7 (0.8)	C30–P–C13	106.6 (0.7)
C30–P–C19	108.1 (0.8)	C1–O1–Mn	110.0 (1.2)
C2–O2–Mn	112.7 (1.3)	C2–C1–O1	117.2 (2.0)
C6–C1–O1	122.8 (2.0)	C6–C1–C2	119.6 (2.1)
C1–C2–O2	114.4 (2.0)	C3–C2–O2	126.7 (2.0)
C3–C2–C1	118.7 (2.1)	C2–C3–Br1	115.9 (1.7)
C4–C3–Br1	122.8 (1.7)	C4–C3–C2	121.1 (2.1)
C3–C4–Br2	118.5 (1.7)	C5–C4–Br2	120.5 (1.8)
C5–C4–C3	121.0 (2.2)	C4–C5–Br3	120.1 (1.9)
C6–C5–Br3	120.7 (1.8)	C6–C5–C4	119.1 (2.2)
C1–C6–Br4	117.8 (1.8)	C5–C6–Br4	122.1 (1.8)
C5–C6–C1	120.1 (2.1)	K–O3–Mn	112.3 (0.6)
C7–O3–Mn	109.1 (1.2)	C7–O3–K	110.8 (1.0)
C8–O4–Mn	107.0 (1.1)	C8–C7–O3	114.0 (1.8)
C12–C7–O3	125.1 (1.8)	C12–C7–C8	120.9 (2.0)
C7–C8–O4	117.2 (1.9)	C9–C8–O4	123.3 (1.9)
C9–C8–C7	119.4 (2.0)	C8–C9–Br5	119.3 (1.7)
C10–C9–Br5	120.2 (1.8)	C10–C9–C8	120.6 (2.1)
C9–C10–Br6	120.7 (1.8)	C11–C10–Br6	119.0 (2.0)
C11–C10–C9	120.2 (2.3)	C10–C11–Br7	123.0 (2.0)
C12–C11–Br7	117.7 (1.7)	C12–C11–C10	119.3 (2.3)
C7–C12–Br8	116.7 (1.6)	C11–C12–Br8	123.7 (1.7)
C11–C12–C7	119.6 (1.9)	P–O5–Mn	163.1 (1.0)

reported for these structures. Chelated octahedral manganese(III) complexes with distorted MnO_6 coordination polyhedra generally have Mn–O lengths that are 0.07 Å longer than values found in the present case.[6] However, Mn(III) complexes that show a strong tetragonal distortion appear to have more comparable in-plane Mn–O lengths. Polymeric *trans*-$[Mn(acac)_2(N_3)]_n$ (acac = acetylacetonate) was shown to have a Mn–L length of 1.910 (1) Å,[7] *trans*-$[Mn(acac)_2(NCS)]_n$ a length of 1.912 (4) Å,[8] and $[Mn(salen)(AcO)]_n$ (salen = *N,N′*-ethylenebis(salicylideneamine)) a length of 1.888 (4) Å to the Schiff base oxygen.[9] *trans*-$Mn(DBCat)_2(py)_2$ has Mn(IV)–O lengths of 1.854 (2) Å and a bite angle of 86.54 (9)°. Catecholate C–O lengths in the present structure average 1.34 (1) Å, a value typically found for catecholate ligands.[10] The triphenylphosphine oxide ligand is bound at an apical site as shown in Figure 1. The Mn–O5 length is 2.135 (15) Å, and the Mn–O5–P bond angle is 163 (1)°. A crystallographic inversion center near the Mn atom generates a second complex anion so that the planar catecholate ligands of adjacent anions are in the dimeric face-to-face orientation shown in Figure 2. The separation between planes of catecholate ligands is approximately 3.3 Å, a value commonly associated with charge-transfer interactions between planar, unsaturated organic molecules. Oxygen O4′ lies 2.71 Å off the plane defined by the atoms of the catecholate ligand containing O1 and O2. Since paired catecholate ligands are not exactly coplanar, atomic contacts increase for atoms furthest from the metal. Catecholate oxygen O4 of the adjacent anion is located at the sixth coordination site of the nominally octahedral Mn atom with a Mn–O4′ length of 2.72 (1) Å.

Potassium cations bridge the two complex anions described above, bonding with O1 and O4 of one anion and O3′ of the adjacent anion. A second inversion center located near the potassium cation and also near the water solvate molecule creates a four-membered ring with two K^+ ions bridged by two water molecules, O6 and O6′. The distorted-octahedral coordination geometry about each potassium is completed by the oxygen atoms of the acetone solvate molecules, O7. The interaction between the dipotassium unit and adjacent dimeric manganese complex units creates a one-dimensional polymeric structure. The repeating unit of this structure is shown in Figure 3.

A crystal of $K[Mn(Cl_4Cat)_2(OPPh_3)]\cdot H_2O\cdot (CH_3)_2CO$ was investigated and found to have the same crystal and molecular

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(6) (a) Fackler, J. P., Jr.; Avdeef, A. *Inorg. Chem.* **1974**, *13*, 1864–1875. (b) Avdeef, A.; Costamagna, J. A.; Fackler, J. P., Jr. *Inorg. Chem.* **1974**, *13*, 1854–1863. (c) Lis, T.; Matuszewski, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1938–1940. (d) Lis, T.; Matuszewski, J.; Jezowska-Trzebiatowska, B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 1943–1946.

(7) Stults, B. R.; Marianelli, R. S.; Day, V. W. *Inorg. Chem.* **1975**, *14*, 722–730.

(8) Day, V. W.; Stults, B. R.; Tasset, E. L.; Day, R. O.; Marianelli, R. S. *J. Am. Chem. Soc.* **1974**, *96*, 2650–2652.

(9) Davis, J. E.; Gatehouse, B. M.; Murray, K. S. *J. Chem. Soc., Dalton Trans.* **1973**, 2523–2527.

(10) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45–87.

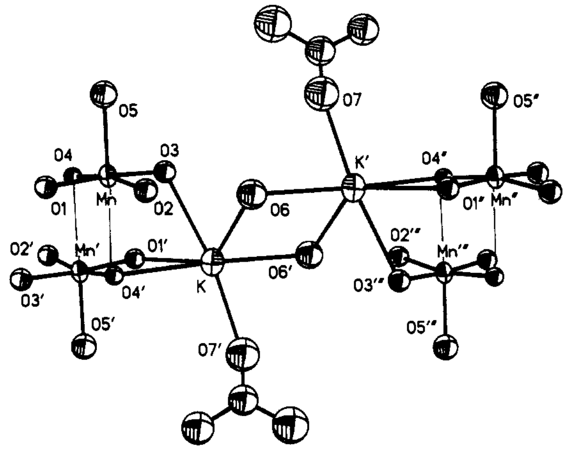


Figure 3. View of the interaction between K^+ ions, the interactions between K^+ ions and complex anions, and the repeating unit defining the crystal structure of $K[Mn(Br_4Cat)_2(OPPh_3)]\cdot H_2O\cdot(CH_3)_2CO$.

structure as the tetrabromocatecholate analogue.

Spectroscopic, Magnetic, and Electrochemical Properties. Infrared spectra recorded on the tetrabromocatecholate and tetrachlorocatecholate complexes are similar. Relatively intense absorptions above 1100 cm^{-1} include bands at 1120, 1240, and 1360 cm^{-1}, which appear associated with the catecholate ligands, triphenylphosphine oxide bands at 1170 and 1425 cm^{-1}, and an acetone absorption at 1780 cm^{-1}.

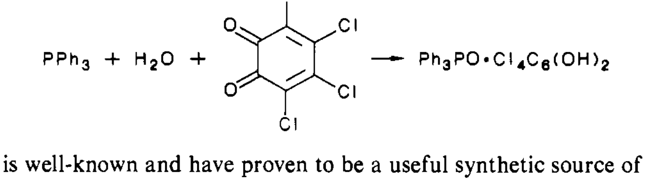
Electronic spectra recorded on complexes with both catecholate ligands in acetonitrile solution are similar. They consist of a low-intensity band at 640 nm (ϵ 110), a stronger band at 340 nm (ϵ 8500), and intense bands at 294 (ϵ 20 000) and 248 nm (ϵ 36 000). Spectra recorded in dichloromethane were identical.

Magnetic measurements carried out on both complexes at room temperature gave values of 4.89 μ_B, close to the spin-only value of 4.90 μ_B commonly found for the high-spin d^4 Mn(III) ion.

The electrochemistry of the tetrachlorocatecholate complex was investigated at scan rates ranging from 0.1 to 4 V/s in both acetonitrile and dichloromethane. No dependence upon scan rate or solvent was observed. The complex shows an irreversible one-electron oxidation at +0.30 V (vs. Fc/Fc^+), which is coupled with a reduction at −0.18 V.

Discussion

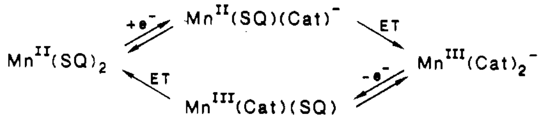
Mechanistic aspects of $Mn(X_4Cat)_2(OPPh_3)^-$ formation by treatment of Mn(II) with triphenylphosphine, catechol, and base were of interest due to the chemistry of Mn(II)–phosphine complexes in reactions with molecular oxygen,[11] reported reactions of manganese catecholate complexes with molecular oxygen,[12] and the potential displacement of O_2 from oxomanganese catecholate complexes in reactions that might provide mechanistic information about metal-catalyzed water oxidation.[4b] However, further investigation of this reaction indicated that the order in which reactants were added was not important and that the products form by two independent redox processes. The reaction between triphenylphosphine and tetrachloro-1,2-benzoquinone to give the triphenylphosphine oxide–tetrachlorocatechol complex



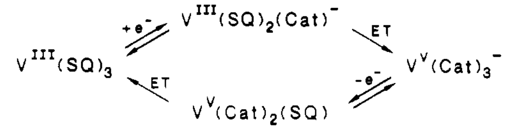
is well-known and have proven to be a useful synthetic source of the catechol.[13] It has also been established that in the presence of basic ligands M(nII) readily undergoes oxidation to Mn(III).[14] These observations combine to give as a reasonable mechanism for complex formation reaction 4, which is closely related to procedure b in the Experimental Section.

$$Mn^{2+} + Ph_3PO\cdot X_4C_6(OH)_2 \xrightarrow{OH^-} Mn(X_4Cat)_2(OPPh_3)^- \quad (4)$$
$$X = Cl, Br$$

Of particular interest in this chemistry is the relationship between the charge distribution in the tetrameric 3,5-di-*tert*-butyl-1,2-semiquinone–manganese(II) complex, $[Mn(DBSQ)_2]_4$, and the $Mn(X_4Cat)_2(OPPh_3)^-$ anion.[4] In the absence of the phosphine oxide ligand the $Mn^{III}(X_4Cat)_2^-$ anion is related to the $Mn^{II}(DBSQ)_2$ unit of the tetramer by a one-electron-oxidation reaction. However, to obtain the charge distribution, $Mn^{II}(SQ)_2$ oxidation must be accompanied by intramolecular metal–quinone electron transfer, giving the result that oxidation of the complex from monoanion to neutral species results in reduction of the metal from Mn(III) to Mn(II).



Reduction of the $Mn(SQ)_2$ unit would likely occur at one of the semiquinone ligands; this would rapidly be followed by intramolecular electron transfer to give the product $Mn(Cat)_2^-$. Electrochemically, oxidation or reduction followed by rapid intramolecular electron transfer would appear as an irreversible EC process and, by the scheme above, would occur at a ligand. Sawyer has reported the electrochemistry of $Mn(DBCat)_2^-$. It shows coupled oxidation and reduction processes on a cyclic voltammogram that is similar in appearance to ours.[3a] The electrochemical processes are shifted to negative potentials relative to ours as would be expected for redox processes occurring at alkyl-substituted catecholate ligands. Similar charge redistribution has been observed for the $V^{III}(Cl_4SQ)_3$ and $V^V(Cl_4Cat)_3^-$ couple



where the one-electron-redox process is accompanied by two-electron transfer between metal and quinone ligands.[15]

Experimental Section

Infrared spectra were recorded as KBr pellets on either a Perkin-Elmer 1330 or a Beckman 4250 spectrometer. Electronic spectra were recorded on a Hewlett-Packard 8451 diode array spectrometer. Magnetic measurements were made by the Faraday method with a Sartorius 4433 microbalance. Electrochemical experiments were carried out with a BAS-100 system. A platinum-wire working electrode and a platinum-coil auxiliary electrode were used. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte a Ag/Ag(Ac) reference electrode was used, and the ferrocene/ferrocenium couple was used as an internal standard.

$K[Mn(O_2C_6Br_4)_2(OPPh_3)]$. (a) Tetrabromo-1,2-benzoquinone (0.42 g, 1.0 mmol) in 15 mL of acetone, triphenylphosphine (0.52 g, 2.0 mmol) in 10 mL of acetone, and KOH (0.112 g, 2.0 mmol) in 5 mL of water were added to a solution of $MnCl_2\cdot 4H_2O$ (0.20 g, 1.0 mmol) in 5 mL of water. The resulting brown solution was heated to reflux for 15 min and reduced in volume. Green-yellow crystals of $K[Mn(O_2C_6Br_4)_2(OPPh_3)]\cdot H_2O\cdot(CH_3)_2CO$ separated from solution in 35% yield. The complex was recrystallized from acetone to give solvated crystals large enough for X-ray analysis. Anal. Calcd for $C_{33}H_{23}O_7MnKPBr_8$: C,

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(11) McAuliffe, C. A.; Al-Khateeb, H. F.; Barrett, D. S.; Briggs, J. C.; Challita, A.; Hosseiny, A.; Little, M. G.; Mackie, A. G.; Minten, K. *J. Chem. Soc., Dalton Trans.* **1983**, 2147–2153.

(12) (a) Chin, D.-H.; Sawyer, D. T. *Inorg. Chem.* **1982**, *21*, 4317–4318 and references therein. (b) Cooper, S. R.; Hartman, J. R. *Inorg. Chem.* **1982**, *21*, 4315–4317.

(13) Holmes, R. R.; Day, R. O.; Sau, A. C.; Holmes, J. M. *Inorg. Chem.* **1986**, *25*, 600–606.

(14) (a) Beagley, B.; McAuliffe, C. A.; Minten, K.; Pritchard, R. G. *J. Chem. Soc., Chem. Commun.* **1984**, 658–659. (b) Boucher, L. J.; Coe, C. G. *Inorg. Chem.* **1975**, *14*, 1289–1295.

(15) Cass, M. E.; Gordon, N. R.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 3962.

Table II. Crystal Data and Details of the Structure Determination for $K[Mn(O_2C_6Br_4)_2(OPPh_3)]\cdot H_2O\cdot(CH_3)_2CO$

Crystal Data	
formula	$KMnBr_8PO_7C_{33}H_{23}$
M_r	1295.83
space group[a]	$P2_1/n$
cryst system	monoclinic
a, Å[b]	10.256 (2)
b, Å	26.434 (3)
c, Å	14.965 (2)
β, deg	102.23 (1)
vol, Å^3	3964.4 (4)
Z	4
d_{calcd}, g cm^{-3}	2.171
d_{exptl}, g cm^{-3}	2.16 (2)
$F(000)$	2464
μ, cm^{-1}	84.98
cryst dimens, mm	0.25 × 0.18 × 0.08
Data Collection and Reduction	
diffractometer	Syntex P$\bar{1}$
data collected	$+h,+k,\pm l$
radiation, Å	Mo Kα (0.71069)
monochromator angle, deg	12.2
temp, K	294–296
scan technique	θ–2θ
scan range (2θ), min–max, deg	3.0–45.0
scan speed, deg min^{-1}	4.0
scan range, deg	0.7 below Kα_1 and 0.7 above Kα_2
bkgd	stationary cryst–stationary counter, bkdg time = 0.5(scan time)
no. of unique reflecns measd	4772
no. of obsd reflecns	1877
criterion	$F > 6\sigma(F)$
abs cor	empirical
transmission factors	0.69–0.22
Structure Determination and Refinement	
programs used	SHELX[c]
scattering factors	neutral atoms[d]
R_1, R_2[e]	0.059, 0.060
weight	$1/(\sigma(F)^2 + 0.0005F^2)$
no. of parameters	260
ratio of observations to parameters	7.22
max shift/error (non-H)	0.58
residual electron density, e/Å^3	0.65

[a] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1965; Vol. 1. [b] Cell dimensions were determined by a least-squares fit of the setting angles of 20 reflections with 2θ in the range 20–30°. [c] Sheldrick, G. M. "SHELX76, a Program for Crystal Structure Determination"; University of Cambridge, Cambridge, England. [d] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 55–60, 99–101, 149–150. [e] The quantity minimized in the least-squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Table III. Atomic Positional and Isotropic Thermal Parameters for $K[Mn(O_2C_6Br_4)_2(OPPh_3)]\cdot H_2O\cdot(CH_3)_2CO$

atom	x	y	z	U_{eq}, Å^2[a]
Mn	0.4834 (3)	−0.0125 (1)	0.1130 (2)	0.031 (2)
K	0.1613 (5)	0.0124 (2)	−0.0821 (4)	0.056 (4)
Br1	0.2494 (3)	0.1092 (1)	0.2748 (2)	0.058 (2)
Br2	0.4622 (3)	0.1972 (1)	0.3761 (2)	0.064 (2)
Br3	0.7804 (3)	0.1856 (1)	0.3709 (2)	0.077 (2)
Br4	0.8774 (3)	0.0895 (1)	0.2547 (2)	0.064 (2)
Br5	0.7330 (2)	−0.1364 (1)	−0.0302 (2)	0.052 (2)
Br6	0.5370 (3)	−0.2356 (1)	−0.0953 (2)	0.078 (2)
Br7	0.2176 (3)	−0.2285 (1)	−0.0870 (2)	0.084 (2)
Br8	0.1057 (3)	−0.1252 (1)	−0.0013 (2)	0.071 (2)
P	0.5311 (7)	−0.0951 (3)	0.3076 (4)	0.042 (4)
O1	0.638 (1)	0.0269 (5)	0.1631 (8)	0.033 (4)
O2	0.390 (1)	0.0343 (5)	0.1712 (9)	0.035 (4)
C1	0.604 (2)	0.0657 (8)	0.210 (1)	0.030 (6)
C2	0.469 (2)	0.0689 (9)	0.218 (1)	0.033 (6)
C3	0.431 (2)	0.1083 (9)	0.266 (1)	0.036 (6)
C4	0.524 (2)	0.1427 (9)	0.311 (1)	0.038 (6)
C5	0.656 (2)	0.1391 (9)	0.307 (1)	0.049 (7)
C6	0.698 (2)	0.0991 (9)	0.259 (1)	0.044 (7)
O3	0.328 (1)	−0.0477 (5)	0.0533 (8)	0.036 (4)
O4	0.572 (1)	−0.0500 (5)	0.0347 (8)	0.024 (4)
C7	0.365 (2)	−0.0912 (8)	0.016 (1)	0.022 (5)
C8	0.500 (2)	−0.0922 (8)	0.010 (1)	0.024 (5)
C9	0.550 (2)	−0.1348 (9)	−0.024 (1)	0.037 (6)
C10	0.467 (3)	−0.176 (1)	−0.054 (2)	0.052 (7)
C11	0.334 (2)	−0.1751 (9)	−0.049 (1)	0.044 (7)
C12	0.283 (2)	−0.1316 (8)	−0.012 (1)	0.027 (6)
O5	0.524 (1)	−0.0675 (6)	0.220 (1)	0.051 (5)
C13	0.430 (1)	−0.0645 (6)	0.376 (1)	0.032 (6)
C14	0.456 (1)	−0.0692 (6)	0.471 (1)	0.064 (8)
C15	0.373 (1)	−0.0456 (6)	0.521 (1)	0.064 (8)
C16	0.264 (1)	−0.0173 (6)	0.477 (1)	0.067 (8)
C17	0.238 (1)	−0.0126 (6)	0.382 (1)	0.078 (9)
C18	0.321 (1)	−0.0362 (6)	0.331 (1)	0.059 (8)
C19	0.702 (1)	−0.0966 (6)	0.3698 (9)	0.033 (6)
C20	0.744 (1)	−0.1302 (6)	0.4422 (9)	0.056 (7)
C21	0.875 (1)	−0.1291 (6)	0.4917 (9)	0.061 (8)
C22	0.965 (1)	−0.0944 (6)	0.4688 (9)	0.062 (8)
C23	0.924 (1)	−0.0608 (6)	0.3965 (9)	0.063 (8)
C24	0.792 (1)	−0.0619 (6)	0.3470 (9)	0.046 (7)
C25	0.477 (2)	−0.1807 (7)	0.207 (1)	0.063 (8)
C26	0.433 (2)	−0.2304 (7)	0.189 (1)	0.10 (1)
C27	0.385 (2)	−0.2579 (7)	0.255 (1)	0.08 (1)
C28	0.381 (2)	−0.2358 (7)	0.339 (1)	0.079 (9)
C29	0.425 (2)	−0.1862 (7)	0.357 (1)	0.067 (8)
C30	0.473 (2)	−0.1586 (7)	0.291 (1)	0.044 (7)
O6	0.111 (2)	0.0089 (6)	0.108 (1)	0.061 (5)
O7	−0.048 (2)	−0.0927 (8)	0.179 (1)	0.088 (6)
C31	0.104 (3)	−0.152 (1)	0.254 (2)	0.10 (1)
C32	−0.152 (3)	−0.168 (1)	0.214 (2)	0.075 (9)
C33	−0.035 (3)	−0.137 (1)	0.212 (2)	0.067 (8)

[a] $U_{eq} = {}^1/_3\sum U_{ii}$.

30.58; H, 1.79; P, 2.63. Found: C, 30.97; H, 2.03; P, 2.48.

(b) Tetrabromocatechol (0.84 g, 2.0 mmol) in 20 mL of ethanol and KOH (0.224 g, 4.0 mmol) in 6 mL of water were added to a suspension of $Mn(OPPh_3)_2Cl_2$ (0.68 g, 1.0 mmol)[16] in 50 mL of acetone. The brown solution was heated to reflux and reduced in volume. Crystals of $K[Mn(O_2C_6Br_4)_2(OPPh_3)]$ were obtained in 73% yield.

$K[Mn(O_2C_6Cl_4)_2(OPPh_3)]$. This complex can be prepared by means of the procedures described above by substituting tetrachloro-1,2-benzoquinone for the tetrabromobenzoquinone in procedure a or tetrachlorocatechol for tetrabromocatechol in procedure b. Spectral data, magnetic moment, and X-ray analysis showed the complex to be analogous with the tetrabromocatecholate complex.

Structure Determination on $K[Mn(O_2C_6Br_4)_2(OPPh_3)]\cdot H_2O\cdot(CH_3)_2CO$. A crystal suitable for crystallographic analysis was mounted on a glass fiber and coated with an amorphous resin to retard loss of the acetone solvate. The crystal was aligned on a Syntex P1 automated diffractometer, and crystal quality was examined with use of rotational and axial photographs. Information regarding the structure determination is given in Table II. Four standard reflections monitored during data collection showed only statistical fluctuations in intensity. The locations of the Mn, P, and Br atoms and several of the lighter atoms were obtained by direct methods with MULTAN, and other atom positions were determined from the phases generated by refinement of these atoms. Fixed contributions for phenyl hydrogen atoms were included with the assumption of idealized positions and a C–H bond length of 0.98 Å. The largest parameter shift on the final cycle of refinement occurred for the thermal parameter of carbon C32 of the acetone solvate molecule with a change of 0.58 relative to its esd. Greatest residual electron density was near Br7 with a value of 0.65 e/Å^3. Final atomic coordinates are given in Table III. Tables containing anisotropic thermal parameters are available as supplementary material.

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Supplementary Material Available: A listing of thermal parameters for $K[Mn(O_2C_6Br_4)_2(OPPh_3)]\cdot H_2O\cdot(CH_3)_2CO$ (2 pages); a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(16) Cotton, F. A.; Goodgame, D. M. L. *J. Chem. Soc.* **1961**, 3735–3741.