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Binuclear Metal Complexes. XLII.[1)] Manganese(IV) Complexes Synthesized by Oxidation of Binuclear Manganese(II) Complexes of 2-(Salicylideneamino)phenols with Tetrachloro-*o*-benzoquinone

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(Received July 24, 1981)

Manganese(IV) complexes Mn(R-R′-sap)$_2$, where H$_2$(R-R′-sap) denotes 2-(salicylideneamino)phenols with the substituent R on the salicylaldehyde ring and the R′ on the *o*-aminophenol ring, were prepared by the oxidation of binuclear manganese(II) complexes Mn$_2$(R-R′-sap)$_2$ with tetrachloro-*o*-benzoquinone (TCOQ). The complexes showed magnetic moments corresponding to three unpaired electrons and strong absorptions in the region 15—20 × 10^3 cm^{-1} attributable to CT transitions. Cyclic voltammograms of Mn(R-R′-sap)$_2$ showed two redox waves which can be interpreted in terms of a two-step reaction, $\mathrm{Mn(IV)} \rightleftharpoons \mathrm{Mn(III)} \rightleftharpoons \mathrm{Mn(II)}$. Both redox potentials of the first and the second processes depend on the substituents R and R′, and there is a good correlation between the redox potentials and Hammett's σ-values of R and R′ to the phenolic oxygen. Mn$_2$(R-R′-sap)$_2$ reacts with TCOQ to give a binuclear manganese(III) complex Mn$_2$(R-R′-sap)$_2$(tcoq), which decomposes in the presence of water forming Mn(R-R′-sap)$_2$.

Manganese is known to play several important roles in biological processes.[2)] Among these, manganese in the photosystem-II has become particularly of interest, where manganese in higher oxidation state functions as a catalyst for oxidizing water to molecular oxygen.[3,4)] The recent findings that two or more manganese ions are involved in the active center of the photosystem-II[5–7)] stimulated interest in binuclear manganese complexes in higher oxidation states (Mn(III) and Mn(IV)).[8,9)] On the other hand, Wang[10)] proposed a mechanism of water oxidation promoted by mononuclear manganese(IV). Thus, much attention is being devoted to synthesis, redox behavior and reactivity of new manganese complexes in higher oxidation state. However, both mononuclear manganese(IV) complexes and binuclear manganese(III) and manganese(IV) complexes seem to be very limited.

Previously, we have reported synthesis, magnetism and structure of binuclear manganese(III) complexes of 3-(salicylideneamino)-1-propanols.[11,12)] As a part of the continuing study on binuclear manganese complexes in higher oxidation state, we brought binuclear manganese(II) complexes of 2-(salicylideneamino)-phenols to reaction with tetrachloro-*o*-benzoquinone (TCQO), in an attempt to prepare binuclear manganese(III) complexes bridged by two phenolic oxygens in the equatorial plane and tetrachlorocatecholate moiety in the apical position. Deep colored products, however, were free from TCOQ and the metal to ligand (2-(salicylideneamino)phenols) ratio was 1 : 2, suggesting the formation of manganese(IV) complexes. In this study, we have characterized the new complexes in terms of magnetic susceptibilities, electronic spectra and cyclic voltammetry. The mechanism of formation of the manganese(IV) complexes has been discussed.

Experimental

Preparations. Ligands employed in this study are the 1 : 1 condensation products of salicylaldehyde or a substituted salicyladehyde and 2-aminophenol or a substituted 2-aminophenol. The ligands are abbreviated as H$_2$(R-R′-sap), in which R and R′ are the substituents on salicylaldehyde and 2-aminophenol, respectively (Fig. 1). Following ligands were used in this study: 2-(salicylideneamino)phenol (H$_2$(sap)), 2-(3-methoxysalicylideneamino)phenol (H$_2$(3-MeO-sap)), 2-(5-methylsalicylideneamino)phenol (H$_2$(5-Me-sap)), 2-(5-bromosalicylideneamino)phenol (H$_2$(5-Br-sap)), 2-(salicylideneamino)-4-chlorophenol (H$_2$(4′-Cl-sap)), and 2-(salicylideneamino)-5-nitrophenol (H$_2$(5′-NO$_2$-sap)). Manganese(II) complexes of H$_2$(R-R′-sap) were prepared by the method described in the literature.[13)]

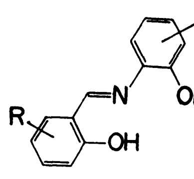


Fig. 1.

Mn(sap)$_2$·1/2H$_2$O. To a suspension of Mn$_2$(sap)$_2$ (266 mg) in methanol (20 cm^3) was added tetrachloro-*o*-benzoquinone (TCOQ) (125 mg) under stirring. The mixture was gently refluxed for 3 h and allowed to stand overnight to give black-purple prisms. They were collected, washed with methanol, and dried over P$_2$O$_5$ *in vacuo*. The yield was 130 mg.

Found: C, 64.23; H, 3.92; N, 5.72%. Calcd for C$_{26}$H$_{18}$N$_2$O$_4$Mn·1/2H$_2$O: C, 64.21; H, 3.94; N, 5.76%.

Mn(3-MeO-sap)$_2$·H$_2$O. A mixture of Mn$_2$ (3-MeO-sap)$_2$ (296 mg) and TCOQ (125 mg) in methanol (20 cm^3) was refluxed for 30 min to give almost black prisms. They were collected, washed with methanol, and dried over P$_2$O$_5$ *in vacuo*. The yield was 75 mg.

Found: C, 60.66; H, 4.55; N, 4.91%. Calcd for C$_{28}$H$_{22}$N$_2$O$_6$Mn·H$_2$O: C, 60.55; H, 4.36; N, 5.04%.

Mn(5-Me-sap)$_2$·1/2H$_2$O. A mixture of Mn$_2$ (5-Me-sap)$_2$ (280 mg) and TCOQ (125 mg) in methanol (20 cm^3) was refluxed for 2 h to give a deep colored solution. To this solution was added dropwise a 1 : 1 mixture of methanol–water (1 cm^3), and stirring was continued for additional 30 min. Almost black prisms thus obtained were collected, washed with a small amount of methanol, and dried over P$_2$O$_5$ *in vacuo*. The yield was 90 mg.

Found: C, 65.11; H, 4.34; N, 5.30%. Calcd for C$_{28}$H$_{22}$N$_2$O$_4$Mn·1/2H$_2$O: C, 65.40; H, 4.53; N, 5.45%.

Mn(5-Br-Sap)$_2$·H$_2$O. This complex was obtained as deep blackish green prisms (80 mg) by the reaction of Mn_2(5-Br-sap)$_2$ (345 mg) with TCOQ (125 mg) in methanol (30 cm^3) for 1 h at room temperature.

Found: C, 47.53; H, 2.53; N, 4.07%. Calcd for $C_{26}H_{16}N_2O_4Br_2Mn \cdot H_2O$: C, 47.81; H, 2.78; N, 4.29%.

Mn(4′-Cl-sap)$_2$·3/2H$_2$O. This complex was prepared as almost black powder (130 mg) by the reaction of Mn_2(4′-Cl-sap)$_2$ (620 mg) and TCOQ (250 mg) in methanol (50 cm^3) for 30 min at room temperature.

Found: C, 54.24; H, 3.09; N, 4.65%. Calcd for $C_{26}H_{16}N_2O_4Cl_2 \cdot 3/2H_2O$: C, 54.47; H, 3.34; N, 4.89%.

Mn(5′-NO$_2$-sap)$_2$·2H$_2$O. This complex was obtained as deep green crystalline powder (150 mg) by the reaction of Mn_2(5′-NO$_2$-sap)$_2$ (620 mg) and TCOQ (250 mg) in methanol (60 cm^3) for 1 h at room temperature.

Found: C, 51.94; H, 3.09; N, 9.65%. Calcd for $C_{26}H_{16}N_4O_8Mn \cdot 2H_2O$: C, 51.93; H, 3.35; N, 9.32%.

Mn$_2$(sap)$_2$(tcoq). A mixture of Mn_2(sap)$_2$ (275 mg) and TCOQ (125 mg) in absolute acetonitrile (25 cm^3) was stirred for 3 h at room temperature in an atmosphere of nitrogen. The reaction was protected from the moisture by means of a VAC Inert Atmosphere and Vaccum Deposition equipment Model HE-43-2. Dark green prisms which separated were collected, washed with acetonitrile, and dried *in vacuo*.

Found: C, 49.23; H, 2.47; N, 3.83%. Calcd for $C_{32}H_{18}N_2O_6Cl_4Mn_2$: C, 49.39; H, 2.33; N, 3.60%.

Ti(sap)$_2$. H_2(sap)$_2$ (2.13 g) was dissolved in absolute methanol (50 cm^3), and to this solution was added $TiCl_4$ (0.95 g) dropwise under stirring. The mixture was stirred for 3 h at room temperature to give red crystals. They were collected, washed with methanol, and dried *in vacuo*.

Found: C, 66.20; H, 3.90; N, 5.90%. Calcd for $C_{26}H_{18}N_2O_4Ti$: C, 66.40; H, 3.86; N, 5.96%.

Measurements. Elemental analyses were performed at the Service Center of Elemental Analysis, Kyushu University. Electronic spectra were recorded on a Shimadzu multipurpose spectrometer Model MPS-5000 in dichloromethane or methanol. Magnetic susceptibilities were measured by the Faraday method. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$.[14] Diamagnetic corrections were made with Pascal's constants[15] and magnetic moments were calculated by the equation, $\mu_{eff}=2.828(\chi_A \times T)^{1/2}$. Cyclic voltammograms were recorded with a Yanagimoto voltammetric analyzer Model 1000. Measurements were made on dichloromethane solutions containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte, using a three-electrode cell. The working electrode is glassy carbon and the auxiliary electrode is platinum coil. The saturated calomel electrode was used as the reference. All the potentials were corrected by the use of ferrocene as an internal standard (Fc^+/Fc: $E_{1/2}=0.400$ V *vs.* NHE[16]).

Results and Discussion

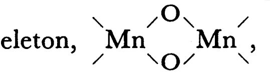
Manganese(II) complexes of H_2(R-R′-sap) were already synthesized,[13,17,18] whose metal to ligand ratio (1 : 1) suggests a polynuclear structure. The 1 : 1 copper(II) complexes with H_2(R-R′-sap) was demonstrated to be binuclear on the basis of magnetic measurements.[19] The two copper(II) ions are supposed to be bridged by the phenolic oxygen atoms of 2-aminophenol, in analogy with the result of X-ray structural analysis of the copper(II) complex for the Schiff base derived from acetylacetone and 2-aminophenol.[20] Thus, it is naturally assumed that the manganese(II) complexes of H_2(R-R′-sap) also possess a binuclear structure bridged by the 2-aminophenol oxygen, hence the complexes being represented as Mn_2(R-R′-sap)$_2$. According to Consiglio *et al.*,[13] the magnetic moments of Mn_2(R-R′-sap)$_2$ are temperature-dependent. For example, they reported that the moment of Mn_2(sap)$_2$ is 5.82 BM at room temperature and 3.89 BM at 140 K. Thus, they presumed an antiferromagnetic spin-exchange interaction operating between a pair of manganese(II) ions. Magnetic properties of Mn_2(R-R′-sap)$_2$ were reexamined in this study in the temperature range 78—300 K. Our measurements revealed that all of the complexes possess a magnetic moment falling in the range 5.8—6.0 BM at room temperature and the moments are almost independent of temperature down to the liquid nitrogen temperature. Magnetic data for Mn_2(sap)$_2$ reported by Consiglio *et al.* can not be interpreted by the susceptibility equation for the (s=5/2)–(s=5/2) system on the basis of the Heisenberg model. We believe that Mn_2(R-R′-sap)$_2$ has a binuclear skeleton, , and spin-exchange interaction between the metal ions is very weak.

TABLE 1. MAGNETIC MOMENTS (μ_{eff}) OF Mn(R-R′-sap)$_2$ AT ROOM TEMPERATURE

Complex	μ_{eff}/BM(T/K)
Mn(sap)$_2$·1/2H$_2$O	3.91(297.3)
Mn(3-MeO-sap)$_2$·H$_2$O	3.94(294.8)
Mn(5-Me-sap)$_2$·1/2H$_2$O	3.96(296.4)
Mn(5-Br-sap)$_2$·H$_2$O	4.03(294.9)
Mn(4′-Cl-sap)$_2$·3/2H$_2$O	4.01(298.0)
Mn(5′-NO$_2$-sap)$_2$·2H$_2$O	4.16(298.1)

Oxidation of Mn_2(R-R′-sap)$_2$ with TCOQ in the open atmosphere resulted in the formation of deeply colored Mn(R-R′-sap)$_2$. Magnetic moments of Mn(R-R′-sap)$_2$ except for Mn(5′-NO$_2$-sap)$_2$·2H$_2$O fall in the range 3.91—4.03 BM (Table 1), which is in good agreement with the moments of the characterized manganese(IV) complexes.[21] Magnetic moment of Mn(5′-NO$_2$-sap)$_2$·2H$_2$O (4.16 BM) is slightly higher than the spin-only value. This may be attributed to the contamination of impurities such as manganese(III) or manganese(II) species. It seems that Mn(sap)$_2$·1/2H$_2$O, Mn(3-MeO-sap)$_2$·H$_2$O and Mn(5-Me-sap)$_2$·1/2H$_2$O are stable in dichloromethane and in the solid state. On the other hand, Mn(5-Br-sap)$_2$·H$_2$O, Mn(4′-Cl-sap)$_2$·3/2H$_2$O and Mn(5′-NO$_2$-sap)$_2$·2H$_2$O are unstable in dichloromethane and amorphous substance precipitates when the solutions are exposed to air for a few hours. Mn(5′-NO$_2$-sap)$_2$·2H$_2$O is particularly unstable and it gradually decomposes in the open atmosphere even in the solid state.

1,2-Naphthoquinone and 9,10-phenanthroquinone do not oxidize Mn_2(R-R′-sap)$_2$. This may be due to the low oxidation potentials of these quinones compared with TCOQ.[22]

TABLE 2. BAND MAXIMA ($\tilde{\nu}/10^3\ cm^{-1}$) AND EXTINCTION COEFFICIENTS (log ε) OF CT BANDS OF $Mn(R\text{-}R'\text{-}sap)_2$

$Mn(sap)_2 \cdot 1/2H_2O$	15.38(3.32), 18.42(3.68), 19.42(3.66)
$Mn(3\text{-}MeO\text{-}sap)_2 \cdot H_2O$	13.50(3.38), 16.21(3.50), 18.02(3.48)
$Mn(5\text{-}Me\text{-}sap)_2 \cdot 1/2H_2O$	15.10(3.36), 18.02(3.69), 18.87(3.69)
$Mn(5\text{-}Br\text{-}sap)_2 \cdot H_2O$	15.15(3.39), 17.95(3.68), 19.05(3.67)
$Mn(4'\text{-}Cl\text{-}sap)_2 \cdot 3/2H_2O$	15.00(3.40), 18.18(3.65), 19.23(3.67)
$Mn(5'\text{-}NO_2\text{-}sap)_2 \cdot 2H_2O$	14.70(3.48), 17.70(3.68), 19.42(3.81)

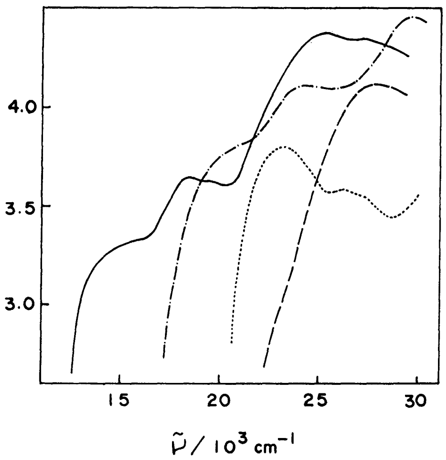


Fig. 2. Electronic spectra of (——) Mn $(sap)_2 \cdot 1/2H_2O$, (– – –) $H_2(sap)$, (------) $Mn_2(sap)_2$, and (–·–) Ti $(sap)_2$.

TABLE 3. CYCLIC VOLTAMMETRIC DATA OF $Mn(R\text{-}R'\text{-}sap)_2$

Complex	E_{pc}	E_{pa}	ΔE_p/mV	$E_{1/2}$
$Mn(sap)_2 \cdot 1/2H_2O$	−0.11 −0.87	−0.01 −0.65	100 220	−0.06 −0.76
$Mn(3\text{-}MeO\text{-}sap)_2 \cdot H_2O$	−0.15 −0.88	−0.05 −0.69	100 190	−0.10 −0.78
$Mn(5\text{-}Me\text{-}sap)_2 \cdot 1/2H_2O$	−0.15 −0.94	−0.04 −0.64	110 300	−0.10 −0.79
$Mn(5\text{-}Br\text{-}sap)_2 \cdot H_2O$	−0.01 −0.73	+0.08 −0.58	90 150	+0.04 −0.66
$Mn(4'\text{-}Cl\text{-}sap)_2 \cdot 3/2H_2O$	0.00 −0.76	+0.08 −0.55	80 210	+0.04 −0.66
$Mn(5'\text{-}NO_2\text{-}sap)_2 \cdot 2H_2O$	+0.18 −0.53	+0.23 −0.45	50 80	+0.21 −0.49

E_{pc} and E_p are calibrated by the use of E_{Fc/Fc^+}[16] and are given in V *vs.* NHE; $E_{1/2}$ is approximated by $E_{1/2} = 1/2(E_{pc}+E_{pa})$.

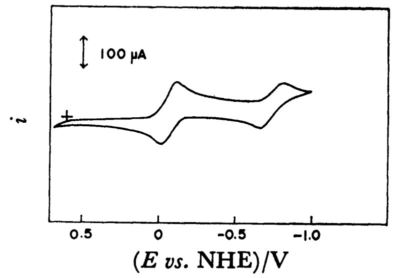


Fig. 3. Cyclic voltammogram of $Mn(sap)_2 \cdot 1/2H_2O$.

Electronic spectra of $Mn(R\text{-}R'\text{-}sap)_2$ were measured in dichloromethane. All the spectra are similar to each other. The spectrum of $Mn(sap)_2 \cdot 1/2H_2O$ is shown in Fig. 2. Figure 2 also includes the spectra of $H_2(sap)$, $Mn_2(sap)_2$ and $Ti(sap)_2$ for comparison. The intraligand transition around $28 \times 10^3\ cm^{-1}$ of $H_2(sap)$ (measured in methanol) shifts to lower frequency and its intensity decreases when it coordinates to a metal. $H_2(sap)$ and $Mn_2(sap)_2$ do not show any strong absorption in the frequency region less than $20 \times 10^3\ cm^{-1}$. On the other hand, $Mn(sap)_2 \cdot 1/2H_2O$ exhibits strong absorptions at $\approx 15 \times 10^3$ and $\approx 19 \times 10^3\ cm^{-1}$, the latter band being composed of two components. The band maxima and the extinction coefficients of these new bands are given in Table 2. These absorptions are too strong to assign to the ligand field bands. Judging from the fact that $Ti(sap)_2$ shows a strong band around $20 \times 10^3\ cm^{-1}$, the 15 and $19 \times 10^3\ cm^{-1}$ bands of $Mn(R\text{-}R'\text{-}sap)_2$ may be assigned to the charge transfer transitions from phenolic oxygens to manganese(IV) ion. Recently, Matsushita *et al.*[23] synthesized manganese(IV) complexes $Mn(R\text{-}X\text{-}sal)_2Cl_2$ of *N*-alkylsalicylideneamines and assigned the strong absorption near $17 \times 10^3\ cm^{-1}$ (log $\varepsilon = 3.5$) to the charge transfer transition $p_\pi(Cl) \rightarrow d_\pi(Mn)$. This band is similar to those of $Mn(R\text{-}R'\text{-}sap)_2$ in frequency and intensity, despite no chloride ion being included in $Mn(R\text{-}R'\text{-}sap)_2$.

Electrochemical properties of $Mn(R\text{-}R'\text{-}sap)_2$ were studied by means of cyclic voltammetry. All of the complexes displayed two redox waves. Cyclic voltammetric data are given in Table 3. Cyclic voltammogram of $Mn(sap)_2 \cdot 1/2H_2O$ is shown in Fig. 3. Electrochemical behaviors of $Mn(R\text{-}R'\text{-}sap)_2$ can be interpreted by the following processes:

$$Mn(IV) \xrightleftharpoons{E^1_{1/2}} Mn(III) \xrightleftharpoons{E^2_{1/2}} Mn(II).$$

The separation between the cathodic and the anodic peaks of the first process is less than 110 mV, indicating a reversible or quasi-reversible redox of this process. The potentials of the first and the second processes, $E^1_{1/2}$ and $E^2_{1/2}$, markedly depend on the substituents R and R′. Complexes containing an electron-withdrawing group, $Mn(5\text{-}Br\text{-}sap)_2 \cdot H_2O$, $Mn(4'\text{-}Cl\text{-}sap)_2 \cdot 3/2H_2O$ and $Mn(5'\text{-}NO_2\text{-}sap)_2 \cdot 2H_2O$, possess higher redox potentials than other complexes. It is evident that an electron-withdrawing group destabilizes the oxidation state of manganese(IV). The substituents R and R′ primarily alter the electron density on the phenolic oxygens. Thus, we plotted the potentials $E^1_{1/2}$ and $E^2_{1/2}$ against the Hammett σ values[24] of R and R′ to the phenolic oxygen (σ_m for $5'\text{-}NO_2$ and σ_p for 5-Me, 5-Br, and 4′-Cl). As is seen in Fig. 4, a good correlation exists between the redox potentials and the substituents of the ligand. The redox potentials of $Mn(3\text{-}MeO\text{-}sap)_2$-

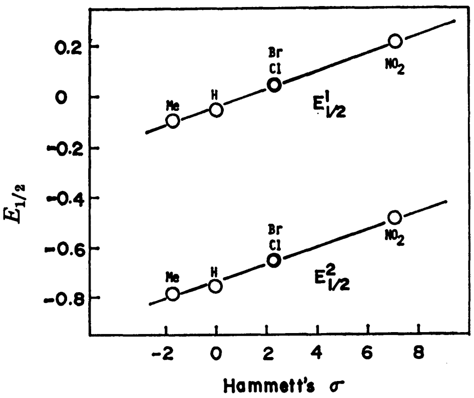
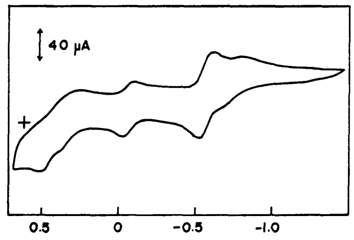


Fig. 4. Correlation between the redox potentials $E_{1/2}$ and $E_{1/2}$ and the Hammett σ values of the substituents R and R′ to the phenolic oxygen for Mn(R-R′-sap)$_2$.

H_2O are comparable to those of Mn(sap)$_2$·1/2H_2O, in spite of the prominent electron releasing ability of methoxy group. This may be interpreted in terms of the "ortho effect."[25]

It is likely that the redox potential of the first process of Mn(5′-NO_2-sap)$_2$·2H_2O (0.21 V. *vs.* NHE) is close to the potential for water oxidation and the instability of this complex must be due to its high redox potential. Similarly, relatively high potentials of Mn(5-Br-sap)$_2$-H_2O and Mn(4′-Cl-sap)$_2$·3/2H_2O ($E^1_{1/2}$=0.04 V) may be responsible for the ready decomposition of these complexes in dichloromethane.

In order to examine the formation mechanism of Mn-(R-R′-sap)$_2$, we brought Mn_2(sap)$_2$ to reaction with TCOQ in acetonitrile under nitrogen atmosphere free from moisture and obtained Mn_2(sap)$_2$(tcoq) as dark green prisms. The magnetic moment of this complex is 4.89 BM at room temperature and 4.80 BM at the liquid nitrogen temperature. Based on the composition and the magnetic moment, we presume that Mn_2-(sap)$_2$(tcoq) is a binuclear manganese(III) complex. Cyclic voltammogram of this complex revealed a redox wave at −0.58 V, which can be attributed to the Mn(III)$\rightleftharpoons$Mn(II) process (Fig. 5). In analogy with the molecular structure of a binuclear manganese(III) complex Mn_2(spa)$_2$(CH_3COO)$_2$ of 3-(salicylideneamino)-1-propanol in which two mangenese(III) ions are bridged by two alcoholic oxygens and two bidentate acetate groups,[12] the most plausible structure for Mn_2(sap)$_2$(tcoq) is given in Fig. 6.



(*E vs.* NHE)/V

Fig. 5. Cyclic voltammogram of Mn_2(sap)$_2$ (tcoq).

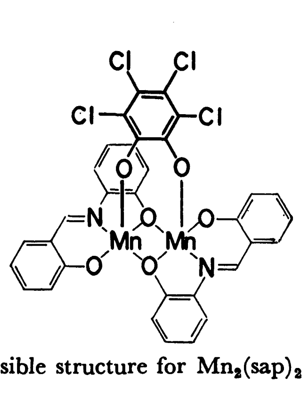


Fig. 6. A possible structure for Mn_2(sap)$_2$(tcoq).

Mn_2(sap)$_2$(tcoq) is very sensitive to water. When water was added dropwise to a methanolic solution of this complex, yellow and blackish purple products were isolated. They were found to be identical with the authentic samples of Mn_2(sap)$_2$ and Mn(sap)$_2$–1/2H_2O, respectively, on the basis of IR spectra. The additional waves at −0.06 and −0.75 V found in cyclic voltammogram of Mn_2(sap)$_2$(tcoq) (Fig. 5) well correspond to the waves of Mn(sap)$_2$·1/2H_2O (Fig. 3 and Table 3). This suggests that Mn_2(sap)$_2$(tcoq) was partly decomposed by the atmospheric moisture to form Mn(sap)$_2$·1/2H_2O. On the basis of these facts, we can represent the reaction between Mn_2(R-R′-sap)$_2$ and TCOQ as follows: Mn_2(R-R′-sap)$_2$+TCOQ$\longrightarrow$ Mn_2 (R-R′-sap)$_2$ (tcoq) $\xrightarrow{H_2O}$ Mn(R-R′-sap)$_2$ Mn_2 (R-R′-sap)$_2$, and others.

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