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Proton Magnetic Resonance Studies on Acetic Acid Exchange at the First Coordination Sphere of Manganese(II)[1]

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Kinetic information on acetic acid exchange at the manganese(II) ion in acetic acid/dichloromethane solution was obtained from the temperature dependence of the solvent proton line broadening and shift. Exactly the same rate for the exchange of the methyl protons and hydroxyl proton of acetic acid indicates that the solvent exchange takes place as a whole acetic acid molecule. The rate constant is $(1.4 \pm 0.7) \times 10^8$ s^{-1} at 25 °C ($\Delta H^* = 42 \pm 3$ kJ mol^{-1} and $\Delta S^* = 50 \pm 15$ J mol^{-1} K^{-1}). These activation parameters are independent of the solvent composition and of the concentration of perchloric acid added to prevent solvolysis of manganese(II). It was suggested that the mechanism of the transverse relaxation of the solvent protons in the first coordination sphere is the dipole–dipole interaction.

Introduction

Acetic acid has the autoprotolysis constant ($K_S = 3.5 \times 10^{-15}$, 25 °C)[2] comparable to that of water and is similar to water for its amphiprotic character. Since acetic acid molecules exist in the state of molecular association[3] due to hydrogen bonding, the dielectric constant of acetic acid is low ($\epsilon = 6.18$, 20 °C).[4] Thus in acetic acid all electrolytes are mainly in the nondissociated form. Kinetic studies on complexation in acetic acid are scarce.[5–7]

The solvent exchange at several transition-metal ions has extensively been studied, mostly by NMR techniques.[8–10] The present work describes a proton NMR study on the manganese(II) ion in acetic acid and in its mixture with dichloromethane or chloroform. This seems to be the first study of acetic acid exchange on (solvato)metal ions in acetic acid.

Experimental Section

Reagents. It is important that all reagents are as dry as possible, since H_2O should strongly solvate metal ions and compete with acetic acid for coordination sites of the metal ions. Therefore extreme care was taken in the purification and preparation of all reagents and compounds. The preparation of acetic acid (HOAc),[11] perchloric acid solution,[5] and hexakis(solvato)manganese(II) perchlorate ($[Mn(HOAc)_6](ClO_4)_2$)[11] was described previously. Chloroform-*d*, dichloromethane-d_2, and tetramethylsilane ($SiMe_4$) were distilled under vacuum over 3A molecular sieves before use.

A solvent sample solution not involving $Mn(ClO_4)_2$ was prepared by distillation of CD_2Cl_2 or $CDCl_3$ and $SiMe_4$ into acetic acid containing perchloric acid. A sample solution containing $Mn(ClO_4)_2$ was prepared by transfer of the same solvent sample solution as obtained above into an NMR tube containing the crystal of $[Mn(HOAc)_6](ClO_4)_2$. All operations for preparation of sample solutions were carried out on a standard vacuum line. The compositions of the sample solutions are tabulated in Table I.

Measurements. The NMR spectra were obtained at 60 MHz on a high-resolution NMR spectrometer (JNM-C-60H, JEOL Ltd.) equipped with a variable-temperature controller (JNM-VT-3C, JEOL Ltd.). The temperature was determined by a thermistor (SPD-02-10A, Takara Thermister Co.) or by a potentiometer (P-1B, Yokokawa Electric Co.) with a copper–constantan thermocouple. The uncertainty of the temperature is estimated to be ±0.3 °C. The ESR spectra were recorded on an ESR spectrometer (ES-SCXA X-band, JEOL Ltd.). $SiMe_4$ (ca. 0.5 wt %) was used as an internal standard for the chemical shift measurement. Care was taken to keep the rf level low enough to avoid saturation. Inert solvents ($CDCl_3$ and CD_2Cl_2) were added to lower the freezing temperature of the solvent and to measure the chemical exchange of acetic acid. The concentration of $Mn(ClO_4)_2$ and the temperature range in our experiments were both limited by the low solubility of $Mn(ClO_4)_2$. The water content of sample solutions was determined by the Karl Fischer titration to be less than 5×10^{-3} *m* (*m* = mol kg^{-1}). The equilibrium constant for aquation of manganese(II) perchlorate in acetic acid is available:[11] $Mn(HOAc)_6(ClO_4)_2 + H_2O \rightleftharpoons Mn(HOAc)_5(H_2O)(ClO_4)_2 + HOAc$, $K = [Mn(ClO_4)_2(H_2O)][Mn(ClO_4)_2]^{-1}[H_2O]^{-1} = 10^{1.26}$. Judging from the value of *K* and the present experimental conditions, we believe with confidence that the presence of water, if any, did not affect our results.

Basic Equations for Treatment of Data. The presentation and analysis of the NMR results given below are based on theories and experimental procedures extensively discussed in the literature.[8,12–14]

The solvent proton NMR line broadening $(T_{2P}P_M)^{-1}$ due to paramagnetic ion is expressed as $(T_{2P}P_M)^{-1} = \pi(\Delta\nu_{obsd} - \Delta\nu_{solv})P_M^{-1}$, where $\Delta\nu_{obsd}$ and $\Delta\nu_{solv}$ (Hz) are the half-height widths of the solvent proton NMR spectra in the presence and absence, respectively, of the paramagnetic ion, T_{2P} is the apparent transverse relaxation time of solvent protons due to the effect of the paramagnetic ion, and P_M is the ratio of the number of solvent molecules bound to the paramagnetic ion to that of free solvent molecules. The value of $(T_{2P}P_M)^{-1}$ depends on the mean lifetime (τ_M s) and the transverse relaxation time (T_{2M} s) of the proton of solvent in the first coordination sphere of the paramagnetic ion, the difference of the resonance frequency between the proton of solvent bound to the paramagnetic ion and that of free solvent ($\Delta\omega_M$ rad s^{-1}), and the relaxation term due to the interaction in the outer sphere of the paramagnetic ion (T_{2O} s). $(T_{2P}P_M)^{-1}$ is derived by Swift and Connick[12,13,15] as

$$\frac{1}{T_{2P}P_M} = \frac{1}{\tau_M}\,\frac{T_{2M}^{-2} + (\tau_M T_{2M})^{-1} + \Delta\omega_M^{\,2}}{(\tau_M^{-1} + T_{2M}^{-1})^2 + \Delta\omega_M^{\,2}} + \frac{1}{T_{2O}} \tag{1}$$

When $\Delta\omega_M$ *is small enough compared with the other relaxation terms,* eq 1 becomes

$$\frac{1}{T_{2P}P_M} = \frac{1}{\tau_M + T_{2M}} + \frac{1}{T_{2O}} \tag{1'}$$

The chemical shift of solvent protons due to the paramagnetic ion is expressed as $\Delta\omega_{obsd}P_M^{-1} = 2\pi(\nu_{obsd} - \nu_{solv})P_M^{-1}$, where ν_{obsd} and ν_{solv} (Hz) are the resonance frequency of solvent protons in the presence and absence, respectively, of the paramagnetic ion. The value of $\Delta\omega_{obsd}P_M^{-1}$ depends on $\Delta\omega_M$, τ_M, and T_{2M}, as given by eq 2.[12]

$$\frac{\Delta\omega_{obsd}}{P_M} = \frac{-\Delta\omega_M}{(1 + \tau_M/T_{2M})^2 + (\tau_M\Delta\omega_M)^2} \tag{2}$$

The usual assumptions, i.e., slow passage, low rf level, and dilute solutions ($P_M << 1$), are made in the derivation of eq 1 and 2. The solvent-exchange rate constant equals $\tau_M^{-1} = (kT/h)\exp(-\Delta H^*/RT$

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Table I. Compositions of Sample Solutions

soln	$[Mn(ClO_4)_2]/m$	$[HOAc]/m$	$[CDCl_3]/m$	$[CD_2Cl_2]/m$	$[HClO_4]/m$	P_M	wt % of HOAc
A0	0	16.65			2.0×10^{-2}	0	100
A1	6.77×10^{-3}	16.65			2.0×10^{-2}	2.45×10^{-3}	100
A2	1.43×10^{-2}	16.65			2.0×10^{-2}	5.18×10^{-3}	100
B0	0	3.11	6.76		1.5×10^{-2}	0	18.7
B1	2.43×10^{-4}	3.11	6.76		1.5×10^{-2}	4.69×10^{-4}	18.7
B2	4.61×10^{-4}	3.11	6.76		1.5×10^{-2}	8.89×10^{-4}	18.7
C0	0	0.91		10.87	2.3×10^{-2}	0	5.5
C1	1.91×10^{-4}	0.91		10.87	2.3×10^{-2}	1.26×10^{-3}	5.5
C2	3.34×10^{-4}	0.91		10.87	2.3×10^{-2}	2.20×10^{-3}	5.5
D0	0	0.38		11.24	2.2×10^{-2}	0	2.3
D1	9.23×10^{-5}	0.38		11.24	2.2×10^{-2}	1.45×10^{-3}	2.3
D2	1.85×10^{-4}	0.38		11.24	2.2×10^{-2}	2.91×10^{-3}	2.3
E0	0	0.89		10.88	1.2×10^{-1}	0	5.4
E1	2.93×10^{-4}	0.89		10.88	1.2×10^{-1}	1.97×10^{-3}	5.4
E2	5.21×10^{-4}	0.89		10.88	1.2×10^{-1}	3.50×10^{-3}	5.4

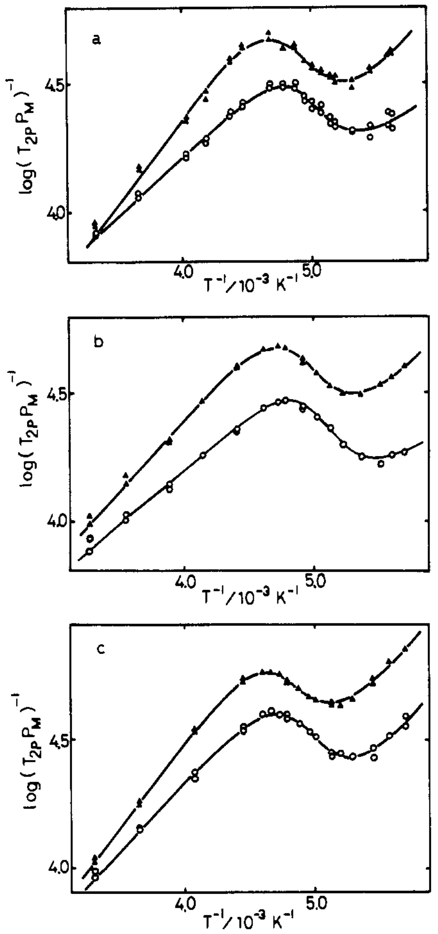

Figure 1. Temperature dependence of $\log(T_{2P}P_M)^{-1}$ for the HOAc methyl protons and hydroxyl proton: a, solution C; b, solution D; c, solution E; O, CH_3 protons; Δ, OH proton. The curves are calculated with parameters obtained.

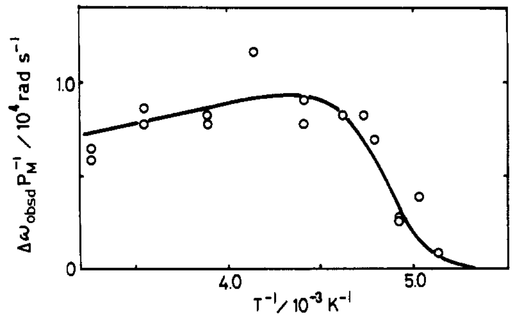

Figure 2. Temperature dependence of $\Delta\omega_{obsd}P_M^{-1}$ for the HOAc methyl protons in solution D. The curve is calculated with the parameters obtained from the data of line broadening.

$+ \Delta S^{\ddagger}/R)$. The temperature dependence of $\Delta\omega_M$ is given by $\Delta\omega_M = -C_\omega/T$.[15] As will be discussed later, T_{2M} is expressed as $T_{2M}^{-1} = (C_M/T) \exp(E_M/RT)$. And T_{2O} is also expressed as the exponential form:[15] $T_{2O}^{-1} = (C_O/T) \exp(E_O/RT)$.

Results

All data for line width $(\pi T_{2P})^{-1}$ and chemical shift $\Delta\omega_{obsd}/2\pi$ are given in the supplementary material.

The temperature dependences of line width $(T_{2P}P_M)^{-1}$ for the HOAc methyl protons and hydroxyl proton in HOAc-inert solvent solutions of $Mn(ClO_4)_2$ are shown in Figure 1. The data for sample solutions A and B are not shown in Figure 1. It was impossible to reduce the temperature low enough to observe solvent-exchange rate due to freezing of solutions A and B. In the present system, P_M is given by $P_M = n[Mn(ClO_4)_2]([HOAc] - n[Mn(ClO_4)_2])^{-1}$, where $[Mn(ClO_4)_2]$ is the concentration of manganese(II) perchlorate and n is the number of acetic acid molecules in the first coordination sphere of the manganese ion. The structure of the crystal of manganese(II) perchlorate has been reported to be octahedrally coordinated by the six acetic acid molecules.[16] It has also been suggested that in acetic acid the manganese(II) perchlorate has the same structure as in crystals and that the perchlorate anion exists in the outer sphere.[11] Thus 6 is accepted for n. Both line width and line shift are proportional to the concentration of $Mn(ClO_4)_2$. The parameters for HOAc methyl protons were computed according to eq 1 by using C_ω fixed at a value (2.4×10^6 K rad s^{-1}) estimated from the high-temperature limiting shift results (vide infra). The resulting parameters showed that eq 1′ expressed satisfactorily the relaxation time in the present systems. A least-squares best-fit treatment[17] of the line-broadening data gives the following parameters: values of $\Delta H^{\ddagger}$/kJ mol^{-1} and $\Delta S^{\ddagger}$/J mol^{-1} K^{-1} for sample solutions C, D, and E are, for methyl protons, 44 and 61, 42 and 54, and 40 and 45, respectively, and, for the hydroxyl proton, 38 and 34, 43 and 58, and 39 and 37, respectively. These values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were not very sensitive to variation in C_ω, C_M, E_M, C_O, and E_O. The values of C_M, E_M, C_O, and E_O in the best fitting are given in supplementary material.

The discrepancy of the activation parameters for chemical exchange in solvents with different composition does not appear to exceed the experimental error. Also the activation param-

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Table II. Activation Parameters for Solvent Exchange on Mn^{2+} in Various Solvents

solvents	k(25 °C)/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/ J mol^{-1} K^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}	nucleus	ref
H_2O	2.1×10^7	33	5.7	-5.4 (25 °C)	^{17}O	19
MBL[a]	2.6×10^4	39	-25		^1H	20
CH_3OH	3.7×10^5	26	-50		^1H	21
				-5.0 (6 °C)	^1H	22
HMPA[b]	1.0×10^7	51	43		^1H	20
Me_2SO[c]	2.7×10^6	37	3		^1H, ^{13}C	23
DMF[d]	2.4×10^6	37	3.1		^1H	20
NH_3	3.6×10^7	33	21		^{14}N	24
CH_3CN	1.2×10^7	30	-7.5		^{14}N	25
HOAc	1.4×10^8	42	50		^1H	this work

[a] *N*-Methyl-γ-butyrolactam. [b] Hexamethylphosphoric triamide. In HMPA the manganese(II) ion exists in tetrasolvato form. [c] Dimethyl sulfoxide. [d] *N,N*-Dimethylformamide.

eters for methyl protons are in agreement with those for hydroxyl proton within the experimental error. The average value of the rate constants for acetic acid exchange was determined to be $(1.4 \pm 0.7) \times 10^8$ s^{-1} at 25 °C ($\Delta H^{\ddagger} = 42 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = 50 \pm 15$ J mol^{-1} K^{-1}).

The temperature dependence of line shift $\Delta\omega_{obsd}P_M^{-1}$ for the HOAc methyl protons is shown in Figure 2. Reliable line shift for the HOAc hydroxyl proton was not observed. Although the HOAc hydroxyl proton may have a line shift as small as for the HOAc methyl protons, the line shift for the former is less precise than that for the latter owing to the former signal being far away from $SiMe_4$ signal. The curve in Figure 2 was calculated from eq 2, by using the same parameters as in the interpretation of the line broadening.

Discussion

Perchloric acid was added to each solution to avoid solvolysis of the manganese(II) ion. There was no effect of perchloric acid on the exchange rate. It should be noted that the exchange rates of the methyl protons and the hydroxyl proton are the same and that the exchange rate is independent of the concentrations of HOAc (The ratio of [HOAc] in sample solutions C and D is 2.4.) and $HClO_4$ (The ratio of [$HClO_4$] in sample solutions E and C is 5.2.). Therefore, it is likely that the exchange takes place as a whole HOAc molecule. The relatively large $\Delta S^{\ddagger}$ value suggests a mechanism with dissociative character, and this is consistent with the exchange rate independent of the concentration of HOAc.

Solvent-exchange rates for manganese(II) ion have been widely studied in a number of solvents. The data[19-25] for solvent exchange on the manganese(II) ion in various solvents are listed in Table II together with ours. Recently Merbach et al. have measured the activation volumes ($\Delta V^{\ddagger}$) for solvent exchange on metal ions by a high-presssure NMR method. According to their data in both methanol[22] and water,[18,19] the positive values of activation volume for Ni^{2+} (smaller than the solvent partial molar volumes) are well in accord with an interchange process with substantially dissociative character (I_d), whereas the negative values for Mn^{2+} (see Table II) were interpreted in terms of an interchange process with considerably associative character (I_a). Thus they have come to the conclusion of a mechanistic changeover from I_a to I_d along the first-row divalent transition-metal ion series (from Mn^{2+} to Ni^{2+}). According to Merbach et al., the exchange of water and methanol on manganese(II) ion seems to be interpreted within the framework of an associative interchange (I_a) mechanism. For acetic acid exchange, on the other hand, the relatively large positive value of entropy (Table II) points to a less associative character of the activation process. For a definite conclusion to be made, a measurement of the activation volume for the exchange of acetic acid on the manganese(II) ion should be required.

The transverse relaxation of a proton nucleus in the first coordination sphere occurs through proton–electron spin–spin dipolar interaction $(1/T_2)_{DD}$[26] and isotropic proton–electron spin exchange $(1/T_2)_{HF}$,[20,27,28] as illustrated by eq 3–8, where

$$\frac{1}{T_{2M}} = \left(\frac{1}{T_2}\right)_{DD} + \left(\frac{1}{T_2}\right)_{HF} \tag{3}$$

$$\left(\frac{1}{T_2}\right)_{DD} = C_{DD}\left(7\tau_{c1} + \frac{13\tau_{c2}}{1 + \omega_s^2\tau_{c2}^2}\right) \tag{4}$$

$$\left(\frac{1}{T_2}\right)_{HF} = C_{HF}\left(\tau_{e1} + \frac{\tau_{e2}}{1 + \omega_s^2\tau_{e2}^2}\right) \tag{5}$$

$$C_{DD} = \frac{1}{15}\,\frac{S(S+1)g^2\beta^2\gamma_I^2}{r^6} \tag{6}$$

$$C_{HF} = \frac{1}{3}\,\frac{S(S+1)A^2}{\hbar^2} \tag{7}$$

$$A = \frac{\Delta\omega_M}{\omega}\,\frac{3kT}{S(S+1)}\,\frac{\gamma_I}{\gamma_S} \tag{8}$$

S is total electron spin of manganese(II) ($^5/_2$), g is the electron g factor, β is the Bohr magneton (erg G^{-1}), γ_I and γ_S are the gyromagnetic ratios of the proton and electron, respectively (rad s^{-1} G^{-1}), r is the electron–proton distance (cm), A is the spin-exchange constant (erg), and ω and ω_s are the resonance angular frequencies of the proton and electron, respectively (rad s^{-1}). The correlation times in eq 4 and 5 are related as follows: $\tau_{c1}^{-1} = \tau_{e1}^{-1} + \tau_r^{-1}$, $\tau_{c2}^{-1} = \tau_{e2}^{-1} + \tau_r^{-1}$, $\tau_{e1}^{-1} = T_{1e}^{-1} + \tau_M^{-1}$, and $\tau_{e2}^{-1} = T_{2e}^{-1} + \tau_M^{-1}$, where τ_r is the correlation time associated with tumbling of the complex ion and T_{1e} and T_{2e} are the longitudinal and transverse relaxation times of the electron, respectively.

The ESR spectra of solution A2 and solution C1 showed six hyperfine lines. T_{2e} was evaluated from the separation of the maximum slopes (35 G), which was experimentally found to be independent of the manganese(II) concentration and of

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the solution composition; we obtained $T_{2e} \simeq 2 \times 10^{-9}$ s at room temperature, which agreed with the reported value for manganese(II) in dilute aqueous solution.[29,30] In our case, ω_s is 2.48×10^{11} rad s^{-1}, and τ_M is about 10^{-8} s at room temperature. Generally, τ_r is nearly equal to 10^{-11} s.[31,32] Therefore, suppose that $T_{1e}^{-1} = T_{2e}^{-1}$; then $(1/T_2)_{HF} = C_{HF}T_{2e}$. With our experimental value of $C_\omega = 2.4 \times 10^6$ K rad s^{-1} for the methyl protons, we obtain $A = 4.6 \times 10^{-22}$ erg and $C_{HF} = 5.5 \times 10^{11}$ s^{-2}. Since the estimated value of $(1/T_2)_{HF}$ is much smaller than the observed value of $1/T_{2M}$, we conclude that $T_{2M}^{-1} = (1/T_2)_{DD}$, i.e. the mechanism of T_{2M} is the dipole–dipole interaction, and also that is the case for the hydroxyl proton. Since there is a linear relationship between log T_{2M}^{-1} and $1/T$ in the higher temperature region as apparent from Figure 1, we can represent T_{2M}^{-1} as an exponential function (vide supra). The electron–proton distance r estimated by using eq 4 is ca. 3.8 Å, which seems to be a reasonable distance. This value is similar to that for the hydroxyl proton since the values of T_{2M}^{-1} for both protons are alike.

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Registry No. HOAc, 64-19-7; Mn, 7439-96-5; $[Mn(HOAc)_6](ClO_4)_2$, 20298-15-1.

Supplementary Material Available: Experimental proton line broadening and proton chemical shift data for $Mn(ClO_4)_2$ in acetic acid and in mixtures with inert solvents (Table sI) and values of C_M, E_M, C_O, and E_O (Table sII) (4 pages). Ordering information is given on any current masthead page.

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Structural Characterization of Tris(3,5-di-*tert*-butylcatecholato)manganate(IV) and Its Redox Reactions with Superoxide Ion

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The disodium salt of the tris(catecholato) complex of manganese(IV), $[Na_2Mn^{IV}(DTBC)_3{\cdot}6MeCN]$, has been synthesized and isolated as dark blue irregular crystals. The structure of the complex, as determined by single-crystal X-ray diffraction methods (hexagonal, $R\bar{3}$; $a = 14.548$ (6) Å, $c = 49.731$ (9) Å; $Z = 6$), is a nearly symmetric octahedral array of oxygen donor atoms (from the three catechol ligands) about the manganese(IV) ion. The proton and ^{13}C NMR spectra for the complex in Me_2SO-d_6 and pyridine-d_5 indicate that it maintains its main structural features in solution. The reactions of the blue $Mn^{IV}(DTBC)_3^{2-}$ complex and its green reduction product, $Mn^{III}(DTBC)_2(H_2O)_2^-$, with superoxide ion in aprotic media have been characterized by spectroscopic, magnetic, and electrochemical studies.

Manganese is an essential cofactor of green-plant photosynthesis in photosystem II for the oxidation of water to dioxygen.[2–4] Another important biological role is as the active catalytic center in mitochondrial and several bacterial superoxide dismutases.[5–7] Apoenzyme that is reconstituted with Fe(II), Co(II), Ni(II), and Cu(II) does not exhibit catalytic activity,[8,9] but reconstitution with $MnCl_2$ restores full catalytic activity.[9] In reactions with photosystem II, manganese appears to serve as an electron-transfer agent in the charge accumulation center of the water oxidizing system. Its other probable role is as a template to bring the oxygen atoms of two water molecules into close proximity to form an O–O bond.[4] Although quinones are present in significant quantities in chloroplasts,[10] they are not effective ligands for transition-metal ions. A model for the manganese cofactor of photosystem II has been proposed that makes use of manganese–catechol complexes as templates for the formation of O–O bonds.[4] This has prompted preparation of stable manganese–catechol complexes to act as effective models for the manganese cofactor of photosystem II and for manganese superoxide dismutases.

In a previous study we observed that molecular oxygen is reversibly bound by the tris(3,5-di-*tert*-butylcatecholato)manganate(IV) complex in aprotic media.[11,12] Because this process is equivalent to the terminal step of the photosystem II oxygen evolution reaction, the structural characterization of the complex and its dioxygen adduct is desirable. The present report summarizes the results of a single-crystal X-ray diffraction study of the tris(3,5-di-*tert*-butylcatecholato)manganate(IV) complex. Its reactions with dioxygen and superoxide ion as well as those for the bis(3,5-di-*tert*-butylcatecholato)manganate(III) complex have been characterized and provide reasonable insight into the mechanism for the

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