REACTION OF DICHLOROMANGANESE(IV) SCHIFF-BASE COMPLEXES WITH WATER AS A MODEL FOR WATER OXIDATION IN PHOTOSYSTEM II

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Abstract—The dichloromanganese(IV) Schiff-base complexes $Mn(N-R-3-NO_2 \text{ sal})_2Cl_2$ ($R = n-C_3H_7$, $n-C_4H_9$, $n-C_6H_{13}$, $n-C_8H_{17}$, $n-C_{12}H_{25}$ and $CH_2C_6H_5$) have been prepared and characterized by magnetic susceptibilities, electronic spectra and cyclic voltammograms. All the manganese(IV) complexes are found to react with water to liberate molecular oxygen(O_2). The maximal liberation of O_2 is observed at neutral pH. The following reaction scheme is proposed:

 $2Mn(IV)(L)_2Cl_2 + 2H_2O \rightarrow 2Mn(II)(L)_2 + O_2 + 4H^+ + 4Cl^-$.

Manganese-containing proteins are believed to play an important role in the photosynthetic oxygenevolving process from water by green algae and green plants.¹⁻³ Although much effort has been made to clarify their function,⁴⁻⁷ the oxidation states of the manganese ions in the proteins, their structures, and the mechanism for water oxidation remain to be established.

Previously, we have reported the preparation and characterization of a series of novel dichloromanganese(IV) Schiff-base complexes.⁸⁻¹⁰ Moreover, we have preliminarily shown that the manganese(IV) complex dichlorobis(*N*-propyl-3-nitrosalicylideneaminato)manganese(IV) reacts with water to liberate molecular oxygen (O_2).¹¹

In this paper we describe the preparation and characterization of a series of dichloromanganese(IV) complexes with bidentate Schiffbase ligands derived from 3-nitrosalicylaldehyde and various monoamines (Fig. 1). All the man-



Fig. 1. Manganese(IV) Schiff-base complexes studied.

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ganese(IV) complexes are found to react with water to liberate O_2 .

EXPERIMENTAL

Materials

All reagents were of reagent grade. Methanol was refluxed over magnesium ribbon and distilled. Dichloromethane was refluxed over CaCl₂ and distilled. 2-Propanol was refluxed over CaO and distilled. Other solvents were purified by the usual methods.

Measurements

UV and visible absorption spectra were obtained from a Hitachi 340 recording spectrophotometer. IR spectra were recorded on a Hitachi EPI-215 and a Hitachi EPI-L grating spectrophotometer for the 4000–650- and 700–250-cm⁻¹ regions, respectively. Mass spectra were measured with a Hitachi RMU-6E spectrometer. Magnetic susceptibilities were measured by the Gouy method at room temperature. Cyclic voltammograms were measured with a Yanaco P-8 polarograph connected with a Yanaco P8-PT potentiostat as described elsewhere.¹⁰ Liberated O₂ in solution was determined by an EIL model 8012-1 oxygen electrode connected with a Yanaco PH 7-1913 voltmeter.



Fig. 2. Apparatus for spectrometric measurement, method 1, and changes in absorbance of pyrogallol solution in the reaction of Mn(IV)(N-Pr-3-NO₂ sal)₂Cl₂ (200 mg) with water (2 cm³).

Procedure for detection and determination of liberated O_2

In the present work, the following two methods were employed to detect and determine O_2 liberated during the reaction of manganese(IV) complexes with water.

Method 1 is based on absorption spectrophotometry using an alkaline pyrogallol solution.¹² The apparatus is shown in Fig. 2. A reaction solvent $[CH_3CN (8 \text{ cm}^3)-H_2O (2 \text{ cm}^3)]$ and a 9 M KOH solution placed in the apparatus were kept completely under a nitrogen atmosphere during all measurements. After nitrogen gas was passed through the reaction system for 1 h, pyrogallol (200 mg) was added to the alkaline solution and dissolved. The solution remained colorless and then the reaction system was sealed. A manganese(IV) complex was added to the reaction solvent, and its mixture was stirred vigorously at room temperature. Its color changed from deep green to yellowish brown, and the pyrogallol solution was colored gradually to dark brown. The color development of the pyrogallol solution was monitored by a spectrophotometer at 420 nm (Fig. 2).

Method 2 is based on the measurement of dissolved oxygen by an oxygen electrode. Dissolved oxygen in a reaction solvent [2-propanol (5 cm³)– H_2O (20 cm³)] was previously determined by the oxygen electrode at 10°C. After a manganese(IV) complex (10 mg) was added to the reaction solvent, the reaction system was sealed. Liberated O₂ was determined by the oxygen electrode as an increase in voltage while stirring the mixed solution at a constant revolution.

Preparation of bidentate Schiff-base ligands

3-Nitrosalicyladehyde was prepared by the method described in the literature.¹³ The Schiff-base ligands were prepared by the condensation of 3-nitrosalicylaldehyde with various monoamines, R-NH₂(R = Pr, Bu, Hx, Oct, Dod and Bz)(see Fig. 1) in tetrahydrofuran. They were recrystallized from appropriate organic solvents such as ethanol and ether. The yields were 65–85%.

Preparation of chloromanganese(III) Schiff-base complexes, Mn(N-R-3-NO₂ sal)₂Cl

A Schiff-base ligand $[N-R-3-NO_2 \text{ salH } (0.02 \text{ mol})]$, manganese(III) acetate dihydrate (0.01 mol) and lithium chloride (0.015 mol) were dissolved in a mixed solvent of methanol (100 cm³) and dichloromethane (100 cm³) and refluxed for 1 h. The mixture was evaporated under reduced pressure to give a dark brown solid. Upon recrystallization from a mixed solvent of dichloromethane and ether, the manganese(III) Schiff-base complex was obtained, washed with 2-propanol, and dried *in vacuo*. The yields were 70–80%. These complexes are soluble in dichloromethane, chloroform and 2-propanol, but insoluble in ether and water.

Preparation of dichloromanganese(IV) Schiff-base complexes, Mn(N-R-3-NO₂ sal)₂Cl₂

Mn(III)(N-R-3-NO₂ sal)₂Cl (2.0 mmol) was dissolved in 2-propanol (100 cm³). A 2-propanol solution of hydrogen chloride (1.5-molar-fold excess over the complex) was added dropwise to the solution of the complex with stirring at room temperature. The mixture changed its color from brown to deep green immediately with a deep green precipitate. After stirring for 30 min, the resulting precipitate was collected on a glass filter, washed with 2-propanol and then ether, and dried in vacuo. Further purification was not carried out. The yields were 25-40%. These manganese(IV) complexes are soluble in dichloromethane, chloroform and acetonitrile, and slightly soluble in methanol and ethanol, but insoluble in ether and water. Their analytical data are given in Table 1.

RESULTS AND DISCUSSION

Electronic absorption spectra

Figure 3 shows the electronic absorption spectra of $Mn(II)(N-Pr-3-NO_2 \text{ sal})_2(H_2O)_2$, $Mn(III)(N-Pr-3-NO_2 \text{ sal})_2Cl$ and $Mn(IV)(N-Pr-3-NO_2 \text{ sal})_2Cl_2$ measured in acetonitrile. The spectrum of the

·	Found (%)					Calc. (%)					
R	с	Н	N	Cl	Mn	С	Н	N	Cl	Mn	
Pr	45.0	4.5	10.2	13.7	10.3	44.46	4.11	10.37	13.13	10.17	
Bu	46.7	4.8	9.8	13.2	9.8	46.49	4.62	9.86	12.84	9.67	
Hx	49.9	5.4	8.7	11.6	8.9	50.00	5.50	8.97	11.35	8.80	
Oct	52.2	6.3	8.4	10.8	8.1	52.93	6.23	8.23	10.42	8.07	
Dod	57.7	7.5	7.0	8.8	6.9	57.56	7.39	7.07	8.94	6.93	
Bz	52.2	3.8	8.8	11.6	8.6	52.84	3.49	8.81	11.14	8.63	

Table 1. Analytical data for the manganese(IV) complexes, Mn(IV)(N-R-3-NO₂ sal)₂Cl₂

manganese(III) complex possesses three absorption bands in the visible region at 16,100, 22,700 and 29,200 cm⁻¹. These bands can be assigned to the transitions due to $d_{xy} \rightarrow d_{x^2-y^2}, d_{xy} \rightarrow \pi^*$ (azomethine) involving d_{yz} , $d_{xz} \rightarrow d_{x^2-y^2}$, and d_{yz} , $d_{xz} \rightarrow \pi^*$ (azomethine) from lower energies.⁸ Similarly, the spectrum of the manganese(IV) complex possesses three absorption bands, which are shifted to higher energies compared with those of the manganese(III) complex. The characteristic band for the manganese(IV) complex observed at 17,200 cm⁻¹ may be assigned to the charge-transfer transition between manganese and chloride ions from its high intensity (log $\varepsilon = 3.4$).⁸ The absorption bands due to d-d transitions for the manganese(IV) complex may be obscured by this intense band, so that the higherenergy bands cannot be assigned certainly, which may be associated with the charge-transfer transitions due to $Mn(d\pi) \rightarrow \pi^*$ (azomethine). On the other hand, the spectrum of the manganese(II) complex has no absorption band in the region lower than 20,000 cm⁻¹ and shows two absorption bands around 25,000 and 28,000 cm⁻¹. These results indicate that the oxidation states of the central manganese ions of the complexes can be easily discriminated from their electronic absorption spectra.



Fig. 3. Electronic spectra in CH₃CN. (----) $Mn(IV)(N-Pr-3-NO_2 sal)_2Cl_2$, (-----) $Mn(III)(N-Pr-3-NO_2 sal)_2Cl$, and (....) $Mn(II) (N-Pr-3-NO_2 sal)_2(H_2O)_2$.

The electronic spectra of the manganese(III) complexes with other alkyl groups are quite similar to that of Mn(III) $(N-Pr-3-NO_2 \text{ sal})_2\text{Cl}$, and those of the manganese(IV) complexes with other alkyl groups also possess absorption bands similar to those of Mn(IV)($N-Pr-3-NO_2 \text{ sal})_2\text{Cl}_2$. The positions of the lowest-energy bands for the manganese(III) and manganese(IV) complexes are summarized in Table 2, together with their intensities. The band position of Mn(IV)($N-Pr-3-NO_2 \text{ sal})_2\text{Cl}_2$ is blue-shifted about 900 cm⁻¹ compared to that of Mn(IV)($N-Pr \text{ sal})_2\text{Cl}_2$ obtained in a previous work.⁸ This may be caused by the introduction of electron-withdrawing nitro groups on the aromatic rings.

Magnetic properties

The magnetic moments of the manganese(III) and manganese(IV) complexes determined at room temperature are summarized in Table 2. The magnetic moments of the manganese(III) complexes fall within the range 4.85-4.98 BM with the exception of Mn(III)(N-Bz-3-NO₂ sal)₂Cl. These values are consistent with the manganese(III) complexes adopting a d^4 high-spin electron configuration. The relatively low value (4.24 BM) observed for Mn(III)(N-Bz-3-NO₂ sal)₂Cl may be caused by magnetic exchange interaction due to the formation of a binuclear structure in the solid state like Mn(III)(N-Bz sal)₂Cl.⁹ Further investigation on this complex was not made in this work.

On the other hand, the magnetic moments of the manganese(IV) complexes fall within the range 3.88-4.02 BM. These values are consistent with the manganese(IV) complexes adopting a d^3 high-spin electron configuration.

IR spectra

The IR spectra of the manganese(IV) complexes are almost the same as those of the corresponding manganese(III) complexes in the 4000-500-cm⁻¹

	0 1	<i>a</i>	ħ	$E_{p/2}$ (vs s		
	Complex R	μ_{eff} (BM)	$v_{\rm max}$ $(10^3 {\rm cm}^{-1}) (\log \varepsilon)$	$Mn(IV) \rightarrow Mr$	$I(III) \rightarrow Mn(II)$	v(Mn-Cl) (cm ⁻¹)
Mn(III)	Pr	4.93	16.13 (2.43)		0.25	
Mn(III)	Bu	4.98	16.03 (2.57)		0.28	
Mn(III)	Hx	4.94	16.23 (2.62)		0.21	
Mn(III)	Oct	4.85	16.10 (2.43)		0.14	
Mn(III)	Dod	4.95	16.18 (2.53)		0.02	
Mn(III)	Bz	4.24	16.18 (2.42)		0.27	
Mn(IV)	Pr	3.96	17.01 (3.46)	1.04	0.28	355
Mn(IV)	Bu	3.99	17.06 (3.42)	0.99	0.25	353
Mn(IV)	Hx	4.02	17.30 (3.43)	0.98	0.18	352
Mn(IV)	Oct	3.88	17.04 (3.73)	0.98	0.11	358
Mn(IV)	Dod	3.97	17.18 (3.47)	0.96	0.15	348
Mn(IV)	Bz	4.01	16.95 (3.41)	0.98	0.22	353

Table 2. Magnetic	moments,	absorption	maxima and	1 reduction	potentials of	of the ma	inganese(III)	and
manganese	(IV) compl	exes, Mn(III)(N-R-3-NO	$_2$ sal) ₂ Cl an	d Mn(IV)(N	-R-3-NO	$_2$ sal) ₂ Cl ₂	

^a Measured at room temperature.

^b Measured in acetonitrile.

^c Measured in acetonitrile containing 0.1 M Bu₄NClO₄ at 25°C.

region. However, in the 500-250-cm⁻¹ region, the IR spectra of the manganese(III) and manganese(IV) complexes differ markedly, especially in the region sensitive to the vibration of v(Mn-Cl). The manganese(III) complexes have weak absorption bands around 310 cm⁻¹, whereas the manganese(IV) complexes have one very sharp and strong absorption band around 350 cm⁻¹ assignable to v(Mn-Cl). The band positions listed in Table 2 are not affected so much by the alkyl groups of the Schiffbase ligands. These results indicate that all the manganese(IV) complexes adopt an octahedral configuration in which two chloride ions occupy a *trans* position about the central manganese ion as shown in Fig. 1.

Electrochemical properties

The current-potential curves of the manganese(IV) complexes measured in acetonitrile exhibit two-step cathodic waves around +1.0 and +0.25 V (vs SCE), which can be assigned to the reductions from Mn(IV) to Mn(III) and from Mn(III) to Mn(II) of the complex, respectively. The reduction potentials for the manganese(IV) complexes are given in Table 2, together with those for the manganese(III) complexes. The potentials for both reductions are not affected much by the alkyl groups of the Schiff-base ligands. These results are consistent with those obtained in the absorption spectra as described above.

It is noteworthy that the manganese(IV) complexes with N-alkyl-3-nitrosalicylideneamines have much more positive reduction potentials than those of the manganese(IV) complexes with N-alkylsalicylideneamines.⁹ This is because the nitro group is one of the strongest electron-withdrawing substituents. Also, the manganese(IV) complexes with 5-nitro analogues have reduction potentials as high as the manganese(IV) complexes with 3-nitro analogues.¹⁰ Such electrochemical properties are considered to be very important with regard to the effective generation of O_2 by oxidative decomposition of water.

Reactivity of the manganese(IV) complexes with water

All the manganese(IV) complexes investigated here are found to react with water based on their color changes from deep green to yellowish brown. These imply that the manganese(IV) species may be reduced to the manganese(III) or manganese(II) species. Thus, we have estimated the reactivity of the manganese(IV) complexes with water by measuring the absorption spectral changes of their acetonitrile solutions $(5 \text{ cm}^3, 2.5 \times 10^{-4} \text{ M})$ caused by addition of water (0.1 cm³). Figure 4 shows the time courses of the relative intensity of the absorbances at the maximal band positions near $17,000 \,\mathrm{cm}^{-1}$ which are characteristic for the manganese(IV) species. It can be seen that the reactivity is affected by the alkyl groups of the complexes: the reaction with water is retarded in the order of $n-C_3H_7 \ll n-C_8H_{17} < n C_{12}H_{25}$). These results indicate that the long-chain alkyl groups such as $n-C_8H_{17}$ and $n-C_{12}H_{25}$ can protect the central manganese(IV) ion from attack by



Fig. 4. Decreases in absorbance at λ_{max} after addition of water to acetonitrile solutions of Mn(IV)(N-R-3-NO₂ sal)₂Cl₂.

water molecules. This may arise from hydrophobicity of these groups. In other words, the reactivity of the manganese(IV) complexes with water can be controlled by the choice of alkyl groups.

Effect of pH of reaction media on quantities of liberated O_2

We have found that the pH values of reaction media decrease in the course of the reaction of the manganese(IV) complexes with water when without buffer solutions. Thus, the pH effect of reaction media on the quantity of liberated O₂ was examined by the use of $Mn(IV)(N-Pr-3-NO_2 \text{ sal})_2Cl_2$. The pH values were adjusted with 0.2 M acetate or 0.06 M phosphate buffer solutions. Figure 5(A) and (B) show the results obtained by methods 1 and 2, respectively. In both cases, the maximal liberation of O₂ was observed in the neutral pH region. This result is particularly interesting in connection with the photosynthetic oxygen evolution by green plants. The decrease in the liberated O_2 in acidic media may result from some decomposition of the manganese(IV) complex by hydrogen ions. On the other hand, the decrease in alkaline media cannot be explained clearly. However, it is supposed that the manganese(IV) complex may form Mn(IV)-OH species which further react with hydroxide ions to give relatively stable Mn(IV)=O species, which are not confirmed in this work.



Fig. 5. Effect of pH on quantity of liberated O₂. (A) Method 1, and (B) method 2.

Table 3. Quantities of molecular oxygen (O_2) liberated during reaction of manganese(IV) complex (20 mg) with water in a mixed solvent of water (20 cm³) and 2-propanol (5 cm³) which was adjusted to pH = 7.0 with a phosphate buffer

Complex R	O ₂ liberated/Mn				
Pr	0.27				
Bu	0.25				
Hx	0.14				
Oct	0.20				
Dod	0.12				
Bz	0.17				

Oxygen liberation by various manganese(IV) complexes

Table 3 shows the quantities of O_2 liberated by the reactions of the manganese(IV) complexes with water at pH 7.0, which were determined by method 2. These values are presented as mol of liberated O_2 per mol of manganese(IV) complex. Among these complexes, Mn(IV)(N-Pr-3-NO₂ sal)₂Cl₂ exhibits the highest value and Mn(IV)(N-Dod-3-NO₂ sal)₂Cl₂ the lowest one. These results can be correlated with the reduction potentials and the reactivities of the manganese(IV) complexes as described above. Therefore, it can be said that the quantity of liberated O₂ depends on the oxidizing power of the manganese(IV) complexes.

Identification of reaction products of manganese(IV) complex with water

The acetonitrile or 2-propanol solution of $Mn(IV)(N-Pr-3-NO_2 sal)_2Cl_2$ changed its color from deep green to yellowish brown on the addition of water. This solution was evaporated under reduced pressure to yield a yellow solid, which was washed with water and dried in vacuo. The analytical data for this reaction product are consistent with the formula $Mn(N-Pr-3-NO_2 sal)_2(H_2O)_2$. Its magnetic moment determined at room temperature is 5.95 BM, indicating that the oxidation state of manganese ion in the reaction product is +II. The electronic spectrum of the product in acetonitrile is identical to that of Mn(II)(N-Pr-3-NO₂ sal)₂(H₂O)₂, which was prepared from manganese(II) acetate tetrahydrate and N-propyl-3-nitrosalicylideneamine. From these results, it is concluded that the manganese(IV) complexes are reduced to their corresponding manganese(II) complexes by reaction with water.

We now propose that the reaction of the manganese(IV) complexes with water proceeds

according to the following equation :

$$2Mn(IV)(L)_2Cl_2 + 2H_2O$$

 $\rightarrow 2Mn(II)(L)_2 + O_2 + 4H^+ + 4Cl^-, (1)$

where L denotes the monoanion of N-alkyl-3nitrosalicylideneamines. The concentration of chloride ions liberated into the reaction solvent was determined by a titration method using a silver nitrate solution. The value obtained was almost equal to that calculated from eqn (1). Moreover, the concentration of hydrogen ions liberated into the reaction solvent, when the reaction was carried out in a medium without buffer solution, was determined by measuring the decrease in the pH value. The value obtained from the pH drop was nearly equal to that calculated from eqn (1).

In order to prove that the liberated O_2 originated from water, isotopic labeled water, $H_2^{18}O$ (20.3 atom %), was used for the reaction solvent. Before reaction, the system and a solvent, 2-propanol (4 cm³) and $H_2^{18}O$ (1 cm³), were degassed under vacuum, and the manganese(IV) complex Mn(IV)(N-Pr-3-NO₂ sal)₂Cl₂ (10 mg) was added to it. After the reaction was complete, the generated gaseous components in the reaction system were analyzed by a mass spectrometer. The mass spectrum thus obtained shows relatively weak peaks at m/z = 36 and 34, in addition to an intense peak at m/z = 32. The former peaks can be assigned to ${}^{18}O^{-18}O$ and ${}^{16}O^{-18}O$, respectively. Although quantitative determination of these species could not be made in this work, it is concluded that the liberated O_2 originated from the water.

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