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Synthesis and electrochemistry of dimanganese(II) complexes of phenol-based dinucleating ligands with four methoxyethyl chelating arms

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ABSTRACT

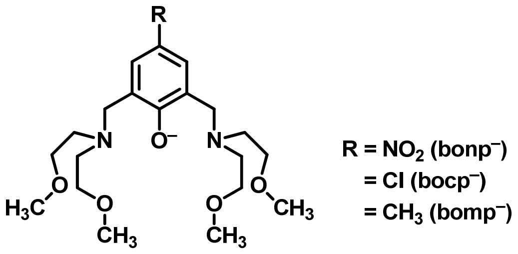
Dimanganese(II) complexes $[Mn_2(bonp)(PhCO_2)_2]PF_6$ (1) and $[Mn_2(bocp)(PhCO_2)_2]PF_6$ (2) were synthesized with *p*-nitro- and *p*-chloro-substituted phenol-based dinucleating ligands bonp$^-$ [2,6-*bis*[*bis*(2-methoxyethyl)aminomethyl]-4-nitrophenolate anion] and bocp$^-$ [4-chloro-2,6-*bis*[*bis*(2-methoxyethyl)aminomethyl]phenolate anion], respectively, with the aim of controlling the redox potentials of the dimanganese center by changing the *p*-substituents in the dinucleating ligands. Cyclic voltammograms of 1 and 2 showed quasi-reversible oxidation processes, assigned to $Mn^{II}Mn^{II}/Mn^{II}Mn^{III}$, at 1.17 and 1.00 V *vs.* Ag/AgCl, respectively. Compared to the previous *p*-methyl complex $[Mn_2(bomp)(PhCO_2)_2]PF_6$ (3) [bomp$^-$: 2,6-*bis*[*bis*(2-methoxyethyl)aminomethyl]-4-methylphenolate anion] (0.96 V *vs.* Ag/AgCl), the order of the potentials was 1(-NO_2) > 2(-Cl) > 3(-CH_3). Thus, the redox potentials of the dimanganese centers were controlled by the *p*-substituents in the dinucleating ligands.

1. Introduction

Dimanganese cores are often seen in biological systems, such as manganese catalases [1-6], manganese ribonucleotide reductase [7], arginase [8], thiosulfate oxidase [9], xylose isomerase [10-12], RNAase [13], and proline aminopeptidase [14], and the dimanganese cores act as the catalytic centers of these enzymes. Some enzymes work as hydrolases, and some work as redox enzymes. For instance, proline aminopeptidase removes the *N*-terminal amino acid by hydrolysis, and manganese catalase catalyzes the disproportionation of H_2O_2 into O_2 and H_2O.

Various types of dimanganese complexes have been prepared as models of the biological systems [15], and the μ-phenoxo-*bis*(μ-carboxylato)dimanganese complex is one of the well-studied dimanganese complexes [16-18]. Previously, we reported a structure and electrochemical properties of dimanganese(II) complexes $[Mn_2(bomp)(PhCO_2)_2]PF_6$ (**3**) and $[Mn_2(bomp)(PhCO_2)_2]BPh_4$ (**4**) [19] [bomp$^-$: 2,6-*bis*[*bis*(2-methoxyethyl)aminomethyl]-4-methylphenolate anion]. In the cyclic voltammogram of **3**, and a quasi-reversible oxidation process was observed at 0.92 V *vs.* SSCE (saturated sodium chloride calomel electrode), assigned to $Mn^{II}Mn^{II}/Mn^{II}Mn^{III}$.

Herein, two new dimanganese(II) complexes $[Mn_2(bonp)(PhCO_2)_2]PF_6$ (**1**) and $[Mn_2(bocp)(PhCO_2)_2]PF_6$ (**2**) have been synthesized with *p*-nitro- and *p*-chloro-substituted phenol-based dinucleating ligands H(bonp) and H(bocp), respectively [H(bonp): 2,6-*bis*[*bis*(2-methoxyethyl)aminomethyl]-4-nitrophenol; H(bocp): 4-chloro-2,6-*bis*[*bis*(2-methoxyethyl)aminomethyl]phenol], with the aim of controlling the redox potentials of the dimanganese center by changing the *p*-substituents in the dinucleating ligands.



Scheme 1

2. Experimental

2.1. Instrumentation

Elemental analyses were obtained at the Elemental Analysis Service Centre of Kyushu University. Infrared (IR) spectra were recorded on a Hitachi 270-50 spectrometer. Cyclic voltammetric measurements were performed using an ALS 400 Electrochemical Analyzer in acetonitrile using a three-electrode cell consisting of a glassy carbon disk working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. Tetra-*n*-buthylammonium tetrafluoroborate ($TBABF_4$) was used as the supporting electrolyte.

2.2. Materials

Na(bonp) [20], Na(bocp) [20], Na(bomp) [21], and complex **3** [19] were prepared according to the methods described in the literature. All other chemicals were commercial products.

2.3. Synthesis

[Mn$_2$(bonp)(PhCO$_2$)$_2$]PF$_6$, **1**: To a methanolic solution (15 mL) of Na(bonp) (0.45 g, 1.0 mmol) was added manganese(II) benzoate tetrahydrate (0.74 g, 2.0 mmol), and the resulting solution was refluxed for 1 h to give a yellow solution. The addition of sodium hexafulorophosfate (0.17 g, 1.0 mmol) resulted in the precipitation of yellow microcrystals. Yield: 0.28 g (30%). Selected IR (KBr, cm^{-1}): 3030-2820, 1605, 1565, 1505, 1450, 1405, 1315, 1085, 1025, 1005, 910, 830, 745, 720, 660, 555, 450. Anal. Calcd. for $C_{34}H_{44}F_6Mn_2N_3O_{11}P$: C, 44.10; H, 4.80; N, 4.55. Found: C, 44.30; H, 4.85; N, 4.60%.

[Mn$_2$(bocp)(PhCO$_2$)$_2$]PF$_6$, **2**: This was prepared as white microcrystals by a method similar to that of **1** using Na(bocp) instead of Na(bonp). Yield: 0.35 g (35%). Selected IR (KBr, cm^{-1}): 3030-2820, 1605, 1565, 1505, 1450, 1405, 1315, 1085, 1025, 1005, 910, 830, 750, 720, 670, 555, 450. Anal. Calcd. for $C_{34}H_{44}ClF_6Mn_2N_2O_9P$: C, 44.65; H, 4.85; N, 3.05. Found: C, 44.45; H, 4.85; N, 3.05%.

2.4. Computations

All the DFT computations were performed using Gaussian 03 software (Gaussian, Inc.) [22-30]. Structural optimization was performed with the B3LYP/LANL2DZ method.

3. Results and discussion

3.1. General properties of complexes 1 and 2

The IR spectra of complexes **1**, **2**, and **3** show the antisymmetric and symmetric $\nu(CO_2)$ vibrations of the benzoate group at 1560~1565 and 1400~1405 cm^{-1}, respectively. A $\Delta\nu$ value [$\Delta\nu = \nu_{as}(CO_2) - \nu_s(CO_2)$] smaller than 200 cm^{-1} is typical of the bridging carboxylate group [31]. The crystal structure of complex **3** was determined previously, and a μ-phenoxo-*bis*(μ-benzoato)dimanganese(II) core was found [19]. Judging from the similarity of the IR spectra, it seems reasonable to assume the μ-phenoxo-*bis*(μ-benzoato) dimanganese(II) structures for both **1** and **2**. Complexes **1** and **2** show no appreciable absorption in the region above 350 nm in DMF solution, and neither does **3**, in accordance with the high-spin d^5 electronic configuration of the manganese(II) ion.

3.2. Electrochemistry

The cyclic voltammograms (CV) of complexes **1** and **2** in acetonitrile solution are shown in Figure 1. In the CV of **2** (Figure 1b), two irreversible waves and one quasi-reversible redox couple were observed: an irreversible reduction wave around –2.4 V, a quasi-reversible first oxidation wave around 1.0 V, and an irreversible second oxidation wave above 1.5 V *vs* Ag/AgCl. These features are very similar to those of **3** reported previously [19] except for a back peak observed at around -1.3 V due to an EC reaction. According to our previous paper, the reduction wave can be assigned to the ligand-based electron transfer process, the first oxidation wave to the $Mn^{II}Mn^{II}/Mn^{II}Mn^{III}$ electron transfer, and the second oxidation wave to the ligand-based electron transfer. In the case of **1** (Figure 1a), in addition to the above-mentioned electron-transfer processes, a quasi-reversible couple is observed around –1.2 V *vs* Ag/AgCl. This wave can be assigned to the reduction of the *p*-nitro group in **1**.

Here we will focus on the first oxidation waves of complexes **1**-**3** for the purpose of investigating the electrochemical properties of the dimanganese centers. In this study, the CV of **3** was again measured using the Ag/AgCl reference electrode because the previous measurement was done using the saturated sodium chloride calomel electrode (SSCE). The first oxidation waves of complexes **1**-**3** are shown in Figure 2, and the electrochemical parameters are summarized in Table 1. The electrochemical behaviors of the complexes are essentially similar to each other. The current parameters I_{pa} are in the range of 730-840 for all the complexes, and these values are consistent for the one-electron processes in acetonitrile solution [32]. Therefore, the first oxidation waves can be assigned to the $Mn^{II}Mn^{II}/Mn^{II}Mn^{III}$ process for all the complexes. The reversibility of the first oxidation waves increased when the scan rate increased, indicating that the first oxidation process is followed by a subsequent chemical reaction (EC mechanism). Judging from the peak current ratio i_{pc}/i_{pa}, the stability of the one-electron-oxidation product of **3** is the highest among the three. In Figure 3, the formal potentials $E^{0\prime}$ for the complexes are plotted against the Hammet's *p*-substituent constants σ_p of the *p*-substituents [33,34] in the complexes. The stronger the electron withdrawing effect [**1** ($-NO_2$) > **2** (-Cl) > **3** ($-CH_3$)], the higher the formal potential [**1** > **2** > **3**]. Thus, the redox potencials of the dimanganese centers are controlled by the *p*-substituents in the dinucleating ligands.

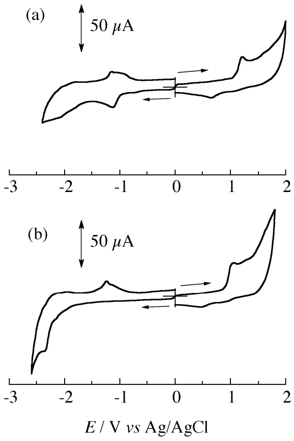


Figure 1. Cyclic voltammograms of **1** (a) and **2** (b) in acetonitrile containing 0.1 M $TBABF_4$ at a glassy carbon disk electrode. (Sweep rate = 0.1 V s^{-1}; Initial direction = positive; Temp. = 25 °C).

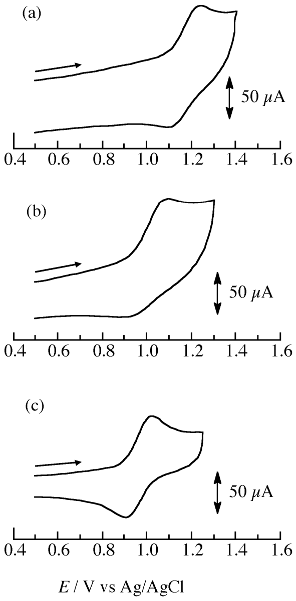


Figure 2. Cyclic voltammograms for the first oxidation processes of **1** (a), **2** (b), and **3** (c) in acetonitrile containing 0.1 M $TBABF_4$ at a glassy carbon disk electrode. (Sweep rate = 1 V s^{-1}; Initial direction = positive; Temp. = 25 °C).

Table 1. Electrochemical parameters of the complexes [a].

Complex	$E^{0\prime}$ / V *vs* Ag/AgCl[b]	*ΔE* /V	I_{pa} / U[c]	i_{pc}/i_{pa}
1	1.17	0.14	731	0.2
2	1.00	0.18	838	0.2
3	0.96	0.12	803	0.6

[a] Sweep rate = 1 V s^{-1}. [b] $E^{0\prime} = (E_{pc} + E_{pa})/2$. [c] U = μA $(mM)^{-1} V^{-1/2} s^{1/2} cm^{-2}$.

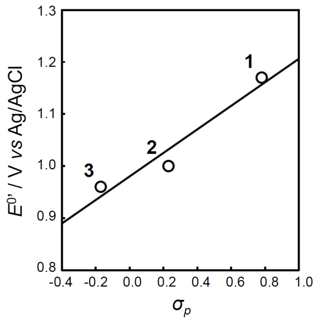


Figure 3. Correlation between the formal potentials $E^{0\prime}$ of the first oxidation processes and the Hammet's parameters σ_p of the *p*-substituents.

3.3. DFT computations

Structures of complex cations for **1**, **2**, and **3** were optimized by DFT method, referring the crystal structure of **3**, and the obtained structures are shown in Figure 4. Since the oxidation potential is related to the HOMO level, the formal potentials $E^{0\prime}$ for the $Mn^{II}Mn^{II}/Mn^{II}Mn^{III}$ processes are plotted against the HOMO level obtained by the DFT computations as shown in Figure 5. A good linearity was observed, and it was better than the plot against the Hammet's constants.

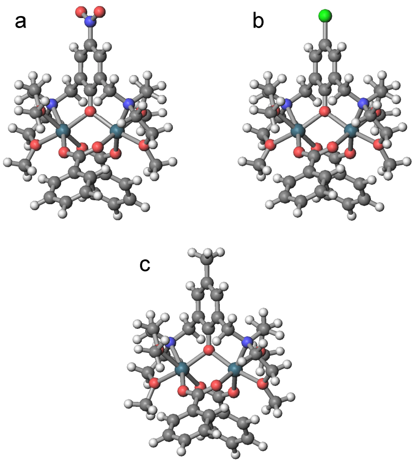


Figure 4. Structures of complex cations for (a) **1**, (b) **2**, and (c) **3**, optimized by the DFT method.

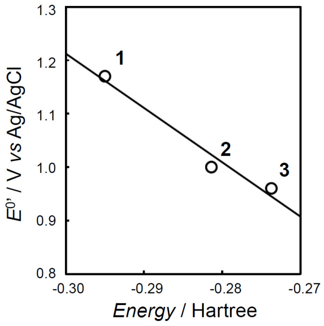


Figure 5. Correlation between the formal potentials $E^{0\prime}$ of the first oxidation processes and the HOMO level.

4. Conclusion

In this study, two new dimanganese(II) complexes have been synthesized using two dinucleating ligands derived from the bomp ligand. It was shown that the redox potential for the $Mn^{II}Mn^{II}/Mn^{II}Mn^{III}$ process was well controlled by the electron-donating/withdrawing effect of the *p*-substituents in the dinucleating ligands.

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