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Synthesis and Characterization of a Dinuclear Manganese(II,III) Mixed Valence Complex with the Dinucleating Ligand, L-py, 2,6-Bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol

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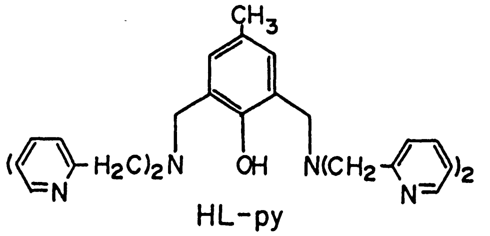
A novel dinuclear manganese(II,III) mixed valence complex, $[Mn_2(L\text{-}py)(CH_3COO)_2](ClO_4)_2 \cdot H_2O$, was prepared by reaction of equimolar amounts of $Mn(ClO_4)_2 \cdot 6H_2O$ and $[Mn(dmso)_6](ClO_4)_3$ with HL-py, CH_3COOH and $(C_2H_5)_3N$ in methanol, where HL-py represents 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol. Cyclic voltammogram in acetonitrile showed two quasi reversible waves at 0.47 V and 1.02 V (vs. SCE), which are assigned to the redox reactions of Mn(II,III)/Mn(II,II) and Mn(III,III)/Mn(II,III), respectively.

Multinuclear manganese site is believed to play an essential role in the water oxidizing system of photosystem II in green plants. Recent developments in this field have revealed that manganese ions exist as dinuclear of tetranuclear site with Mn-Mn distances of approximately 2.7 Å and that the II, III, and/or IV oxidation states of manganese ions are involved in the catalytic cycle of water oxidation.[1)] However, details of structure and the reaction chemistry of multinuclear site still remain ambiguous. For an advanced


HL-py

Scheme 1.

elucidation of the nature of multinuclear manganese site, it is needed to clarify the coordination chemistry of dinuclear and tetranuclear manganese complexes in various oxidation states which have biologically relevant ligands such as imidazole, carboxylate, phenolate, etc.

In this study, we report the synthesis and some physicochemical properties of a novel dinuclear manganese(II,III) mixed valence complex, $[Mn_2(L\text{-}py)(CH_3COO)_2](ClO_4)_2 \cdot H_2O$, where HL-py is 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol[2] (Scheme 1). Such dinuclear manganese(II,III) mixed valence complexes are quite rare,[3] although dinuclear manganese(III,IV) mixed valence complexes have been extensively studied.[4]

The complex was prepared by reaction of $Mn(ClO_4)_2 \cdot 6H_2O$ (1 mmol) and $[Mn(dmso)_6](ClO_4)_3$ (1 mmol) with HL-py (1 mmol), CH_3COOH (2 mmol), and triethylamine (2 mmol) in methanol. Found: C, 45.47; H, 3.90; N, 8.31; Mn^{III}, 5.4[5] and 5.8;[6] Mn(total), 10.8%.[7] Calcd for $C_{37}H_{39}N_6O_5(ClO_4)_2Mn_2 \cdot H_2O$: C, 45.60; H, 4.24; N, 8.62; Mn^{III}, 5.64; Mn(total), 11.27%. It was attempted to prepare dinuclear manganese(III,III) complex by reaction of $Mn(CH_3COO)_3 \cdot 2H_2O$ with HL-py and $NaClO_4$ in methanol or ethanol. However, the above mixed valence complex was exclusively isolated in ca. 50% yield. This indicates that at least twenty five percent of manganese(III) ion is reduced in the above reaction conditions. It seems likely that methanol or ethanol functions as reducing agent.

Quantitative analyses of manganese(III) ion by the two methods[5,6] gave close analytical results and suggest that the complex contains only one manganese(III) ion. Molar conductivity in acetonitrile is 225 Ω^{-1} cm^2 mol^{-1}, indicating the presence of a 2 : 1 electrolyte. From the dinucleating nature of L-py and elemental analysis as well as molar conductivity, it may be concluded that the complex can be formulated as $[Mn_2(L\text{-}py)(CH_3COO)_2](ClO_4)_2 \cdot H_2O$.

The magnetic moment of the complex is 7.1 B.M./2Mn at room temperature. This suggests that both manganese(II) and (III) ions are in high spin state (S=2 and S=5/2, respectively). The magnetic susceptibilities were also measured over the temperature range 80 - 300 K. The results were analyzed with the spin-spin interaction Hamiltonian, $\mathcal{H} = -2JS_1 \cdot S_2$. The molar susceptibility (χ_A) of an $S_1=2$ — $S_2=5/2$ exchange coupling dimer is given by the following equation:

$$\chi_A = \frac{N\beta^2 g^2}{4kT} \frac{x^{24} + 10x^{21} + 35x^{16} + 84x^9 + 165}{x^{24} + 2x^{21} + 3x^{16} + 4x^9 + 5}$$

where $x=\exp(-J/kT)$ and the symbols have their usual meanings. The experimental values are well interpreted in terms of the above equation as can be seen in Fig. 1, where the solid line is a calculated curve by using the following parameters, $J=-6.1$ cm^{-1} and $g=2.00$. This also supports the presence of high spin manganese-(II) and (III) ions in 1 : 1 molar ratio in the dinuclear unit. Manganese(II) and (III) ions are antiferromagnetically coupled to yield $S=1/2$ ground state. Such weak antiferromagnetic exchange interaction has also been observed in the dinuclear high spin iron(II,III) mixed valence complexes with L-py such as [Fe$_2$-(L-py)(CH$_3$COO)$_2$](BF$_4$)$_2$•H$_2$O and analogous complexes ($J=-3.2$ - -8.0 cm^{-1}).[8)]

In order to investigate the electrochemical property, cyclic voltammogram was measured in acetonitrile containing ca. 0.1 mol dm^{-3} $(n\text{-}C_4H_9)_4NClO_4$ at a glassy carbon electrode by using an SCE as reference electrode. As can be seen in Fig. 2, the complex exhibits two quasi reversible redox waves at 0.47 and 1.02 V (vs. SCE). These two sets of the redox waves may correspond to two stepwise one electron transfer: the former is assigned to Mn(II,III)/Mn(II,II) and the latter Mn(III,III)/Mn(II,III), respectively. From the separation of two redox potentials (0.55 V), the conproportionation constant (K) may be roughly estimated for the following equilibrium at 25 °C:

$$\text{Mn(III)-Mn(III)} + \text{Mn(II)-Mn(II)} \xrightleftharpoons{K} \text{2Mn(II,III)}$$

The value obtained is 1.7×10^9, indicating that the present mixed valence complex is considerably stabilized. A large asymmetry of two manganese sites in the redox

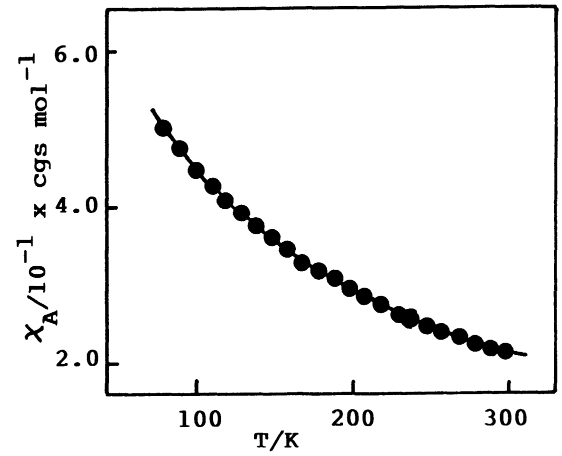


Fig. 1. Temperature dependence of magnetic susceptibilities of [Mn$_2$-(L-py)(CH$_3$COO)$_2$](ClO$_4$)$_2$•H$_2$O.

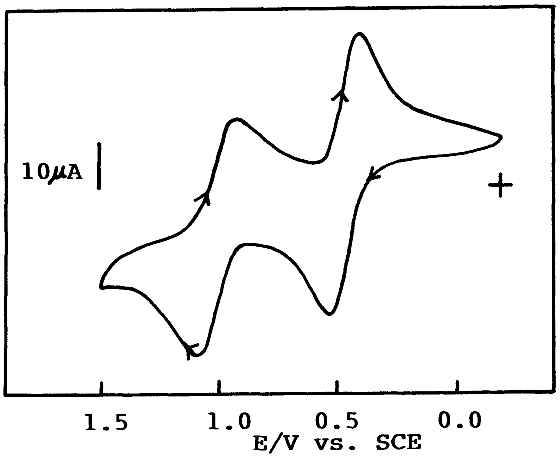


Fig. 2. Cyclic voltammogram of [Mn$_2$(L-py)-(CH$_3$COO)$_2$](ClO$_4$)$_2$•H$_2$O in acetonitrile. The scan rate is 100 mV s^{-1}.

behavior may partly come from a structural asymmetry, although both manganese sites have N_3O_3 donor set. In fact, some structural asymmetry in two metal sites was already found in the dinuclear cobalt and the dinuclear copper complexes with L-py.[9,10]

The complex shows two intense absorption bands at 16100 cm^{-1} (ε=810 mol^{-1} dm^3 cm^{-1}) and 20800 cm^{-1} (ε=1160 mol^{-1} dm^3 cm^{-1}) in acetonitrile. They are tentatively assigned to the d-d transitions of manganese(III) and/or charge transfer transitions of phenolate to half filled $d\pi^*$ of manganese(III) ion. It should be noted that no intervalence charge transfer band (IT band) is observed in the visible and near infrared region, although the corresponding iron(II,III) mixed valence complex mentioned previously showed an intense IT band in the near infrared region.[8] This suggests that the present manganese mixed valence complex consists of valence trapped manganese(II) and (III) ions. Further studies of such type of dinuclear manganese complexes are in progress.

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