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Synthesis and Characterization of the Di(μ-oxo)Dimanganese(III,IV) Complex with Carboxylato Groups as a Terminal Ligand

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A dinuclear manganese(III,IV) mixed valence complex $[Mn_2(N_3O\text{-py})_2(O)_2]ClO_4\cdot 2.5H_2O$ was prepared (N_3O-py:N,N-bis(2-pyridylmethyl)glycinate) and its crystal structure was determined by X-ray crystal structure analysis. The analysis showed that two manganese ions are linked by two oxo bridges with the separation of 2.656(2) Å and the structural difference between manganese(III) and manganese(IV) moieties is relatively small compared to those of complexes so far reported.

The tetranuclear manganese center in photosystem II (PSII) in green plants has been shown to play an essential role in oxidation of water to molecular oxygen.[1-3] Recent ESR studies of the S_2 state in PSII suggested that the S_2 state is in the mixed valence state of manganese(III) and manganese(IV) ions, and consists of two dinuclear di(μ-oxo)-dimanganese cores ($2[Mn_2(O)_2]$).[2,3] In addition, EXAFS studies pointed out that nitrogen and/or oxygen atoms participate in acting as terminal ligand atom(s) around the $[Mn_2(O)_2]$ core.[4,5] Recently several di(μ-oxo)-dimanganese(III,IV) complexes with a terminal N_4 donor set have been reported as model complexes for the S_2 state.[6-12] The di(μ-oxo) or μ-oxo complexes with additional carboxylato bridge(s) have also been devised.[13] However, there is no dinuclear manganese(III,IV) mixed valence complex containing terminal oxygen donor atom(s). Thus it is very interesting to investigate electrochemical, magnetic, and spectroscopic properties of a dinuclear mixed valence manganese(III,IV) complex with terminal oxygen donor(s) such as a carboxylate which is the most probable oxygen donor in manganese proteins. In the previous study, we reported the synthesis, magnetic and electrochemical properties of manganese(III,IV) and (IV,IV) complexes with a tripod ligand (N_4 donor set).[10] As an extension of our study on dinuclear complexes,[10,14] here we report the synthesis of a dinuclear manganese(III,IV) complex with a tripod-like carboxylato ligand (N_3O donor set), $[Mn_2(N_3O\text{-py})_2(O)_2]ClO_4\cdot 2.5H_2O$, its crystal structure, and some physicochemical properties, where N_3O-py is N,N-bis(2-pyridylmethyl)-glycinate.

The ligand, HN_3O-py, was synthesized by the reaction of bis(2-pyridylmethyl)-amine with bromoacetic acid at pH 10. The complex was prepared as follows: To a solution of HN_3O-py (1 mmol) and $Mn(NO_3)_2 \cdot 4H_2O$ (1 mmol) in 30 cm^3 of H_2O was added a few drops of 35% H_2O_2. The pH of the solution was adjusted to ca. 7 by adding an aqueous solution of $NaHCO_3$ and then ammonium perchlorate was added to the resulting dark green solution. The solution was allowed to stand overnight to give dark green crystals. Recrystallization was achieved from acetonitrile-water (1 : 1). Found: C, 41.88; H, 4.25; N, 10.54%. Calcd for $Mn_2C_{28}H_{28}N_6O_6$-$(ClO_4) \cdot 2.5H_2O$: C, 42.09; H, 4.16; N, 10.52%.

A dark green crystal of square pyramidal shape with dimensions of 0.2 x 0.2 x 0.2 mm^3 was used for X-ray crystal structure analysis. Crystal data: $[Mn_2(N_3O\text{-py})_2(O)_2]ClO_4$ $2.5H_2O$: F.W=798.93, orthorhombic, $Pna2_1$, a=14.083(1), b=10.892(1), c=21.477(4) Å, V=3294.4(7) $Å^3$, Z=4, Dm=1.60, Dc=1.61 g cm^{-3}, μ(Mo-Kα)=5.99 cm^{-1}. Intensity data were collected by a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromated Mo-Kα radiation and corrected for Lorentz-polarization effects. A total of 4284 reflections with 2θ<55° were obtained, of which independent 2677 reflections with $|F_o| > 3\sigma|F_o|$ were used for the structure determination. The structure was solved by the direct method and refined by the block-diagonal least-squares method. The calculations were carried out with the TEXRAY Structure Analysis software package on ciroVax II and with the UNICS III programs[15,16] on a FACOM 760/10 computer at the Kanazawa University Information Processing Center. The current residual value was R=0.057.

Figure 1 shows the molecular structure of the complex cation with selected bond distances and angles. Two manganese ions are bridged by two oxo groups with the separation of 2.656(2) Å and in distorted octahedral geometries with a cis,cis-N_3O_3 donor set. The accuracy of the present results is somewhat unsatisfactory because of serious disorder of the perchlorate anion. However, the Mn(III) and Mn(IV) ions are distinguishable from a comparison

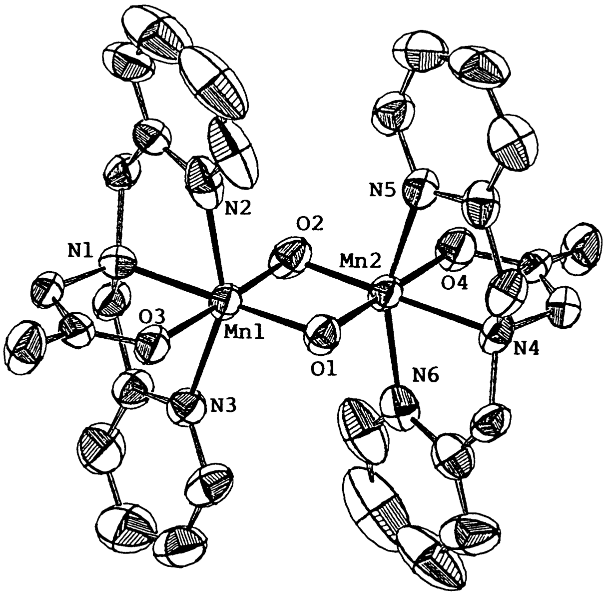

Fig. 1. Molecular stucture of $[Mn_2(N_3O\text{-py})_2(O)_2]^+$ cation and selected bond distances (l/Å) and angles (φ/°): Mn1-Mn2 2.656(2), Mn1-O1 1.818(7), Mn1-O2 1.822(7), Mn1-O3 1.963(8), Mn1-N1 2.071(8), Mn1-N2 2.174(11), Mn1-N3 2.173(9), Mn2-O1 1.814(7), Mn2-O2 1.784(7), Mn2-O4 1.956(8), Mn2-N4 2.080(9), Mn2-N5 2.107(9), Mn2-N6 2.107(9); Mn1-O1-Mn2 94.0(3), Mn1-O2-Mn2 94.9(3).

of the axial bond distances at manganese ions. The Mn1-N2 and Mn1-N3 distances (axial bond: 2.174(11) and 2.173(9) Å) are apparently longer than those at Mn2 (Mn2-N5: 2.107(9) and Mn2-N6: 2.107(9) Å), although there is little difference in the in-plane bond distances at Mn1 and Mn2. The coordination geometry at Mn1 may be best described as an elongated octahedron, which is predicted by the Jahn-Teller distortion of a high spin d^4 Mn(III) ion. Recent EXAFS study of the Mn complex of PSII treated with $CaCl_2$ suggested the presence of N or O at 1.92 Å.[4)] The Mn-O (terminal oxygen) distances in the present complex are 1.963(8) and 1.956(8) Å, which support the presence of a terminal oxygen donor atom in the above Mn complex in PSII. The differences in bond distances at Mn1 and Mn2 are relatively small compared with those in the phen(1,10-phenanthroline), tren(tris-(2-aminomethyl)amine), and N_4-py(tris(2-pyridylmethyl)amine) complexes,[7,9,11)] although a similar small difference was also observed for the bispicen(N,N'-bis-(2-pyridylmethyl)ethylenediamine) complex.[8)]

The magnetic susceptibility was measured over the temperature range 80 - 300 K. The data were fitted to the isotropic spin exchange Hamiltonian $\mathcal{H}=-2JS_1\cdot S_2$ ($S_1=2$ and $S_2=3/2$) with parameters $J=-151$ cm^{-1}, $g=2.00$, TIP=100 x 10^{-6} emu mol^{-1}, and impurity=0.1% as a monomeric manganese(III) complex. Such magunitude of antiferromagnetic interaction between Mn(III) and Mn(IV) was also observed for $[Mn_2(N_4\text{-py})_2(O)_2](ClO_4)_3\cdot 2.5H_2O$ (-159 cm^{-1})[10)] and other complexes (-134 - -150 cm^{-1}).[6,11)]

The frozen solution ESR spectrum showed a sixteen ^{55}Mn hyperfine pattern at g≈2 (Fig. 2). Such a sixteen hyperfine pattern at g≈2 is expected for an antiferromagnetially coupled Mn(III,IV) dimer with a spin state of 1/2 where two manganese ions are not equivalent. Preliminary computer simulation of the multiline spectrum yielded the spectral parameters: g_z= 1.995, g_{xy}= 2.000, A_{z1}=130 x 10^{-4} cm^{-1}, A_{xy1}=150 x 10^{-4} cm^{-1}, and $A_{z2}=A_{xy2}$=70 x 10^{-4} cm^{-1}. The ESR results indicate that the complex is in a trapped mixed valent state.

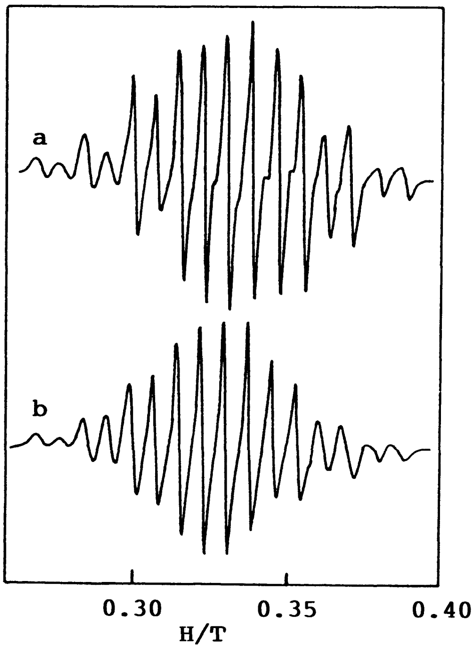

Fig. 2. ESR spectrum of the complex in DMF-toluene-ethanol(1 : 1 : 1) at 15 K (a) and a simulated spectrum (b) obtained with the parameters described in the text.

Cyclic voltammetry exhibited two sets of reversible redox waves at 0.76 and -0.02 V vs. SCE in acetonitrile (ferrocene was used as an internal standard, whose $E_{1/2}$ was 0.39 V vs. SCE). The former corresponds to the redox couple of Mn(IV,IV)/Mn(III,IV) and the latter Mn(III,IV)/Mn(III,-III). The corresponding $E_{1/2}$ values of $[Mn_2(N_4\text{-py})_2(O)_2]^{3+}$ are 1.04 and 0.24 V vs. SCE in acetonitrile.[10)] It should be noted that the introduction of one carboxylato group as a terminal ligand significantly lowered the redox potentials of dimer (0.30 - 0.25 V). Thus the carboxylato group may be useful to adjust the redox potential of the manganese complex suitable for water oxidation. $[Mn_2(phen)_2(O)_2]^{3+}$ has been shown to have catalyic activity for water oxidation in the presence of Ce(IV) ions.$^{17)}$ However the present complex did not show such oxidation under similar conditions and decomposed to evolve CO_2 in 0.1 M HCl solution. Further studies of oxidation reactions are in progress.

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