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Synthesis and Characterization of a Novel Tetranuclear Manganese(II,III,III,II) Mixed Valence Complex

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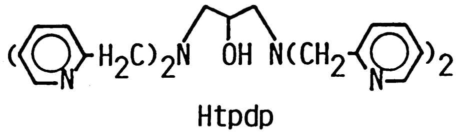
A novel tetranuclear manganese(II,III,III,II) mixed valence complex $[Mn_4(tpdp)_2(CH_3COO)_2(O)(H_2O)_2](CF_3SO_3)_4\cdot 2H_2O$ was prepared, where Htpdp is N,N,N',N'-tetrakis(2-pyridylmethyl)-1,3-diamino-2-propanol, and its crystal structure was determined by X-ray structure analysis. The complex cation consists of two dinuclear manganses(II,III) mixed valence units with alcholato and acetato bridging groups and those two dinuclear units are linked by oxide ion bridging manganese(III) moieties, forming a linear tetranuclear structure (Mn_4(II,III,III,II)).

The tetranuclear manganese center in photosystem II (PSII) in green plants has been shown to play an essential role for catalytic oxidation of water to molecular oxygen.[1)] In the catalytic cycle, manganese ions undergo various oxidation states, di-, tri-, and tetravalent. However, little is known on the structure of the manganese center and the reaction mechanism of water oxidation. Therefore, it is necessary to investigate polynuclear manganese complexes with various oxidation states. A variety of tetranuclear mixed valence complexes of manganese have been reported as models for the manganese center in PSII.[2)] As a part of our current studies on the polynuclear manganese mixed valence complexes, here we report the synthesis of a novel linear tetranuclear manganese(II,III,III,II) complex with N,N,N',N'-tetrakis(2-pyridylmethyl)-1,3-diamino-2-propanolate (tpdp), $[Mn_4(tpdp)_2(CH_3COO)_2(O)(H_2O)_2](CF_3SO_3)_4\cdot 2H_2O$, its crystal structure, and magnetic properties.


Htpdp

Htpdp was prepared by the reaction of a mixture of 1,3-diamino-2-propanol dihydrochloride with pyridine-2-aldehyde in methanol with $NaB(CN)H_3$. The ligand was purified by silica gel chromatography with methanol as an eluent.

To a solution of Htpdp (0.5 mmol), $CH_3COONa \cdot 3H_2O$ (1 mmol), and CH_3COOH (0.5 mmol) in 30 cm^3 of ethanol-water (1 : 1) was added $Mn(CH_3COO)_2 \cdot 4H_2O$ (1 mmol) under stirring. To the mixture, a few drops of 35% H_2O_2 was added to oxidize manganese(II) ions and then CF_3SO_3Na (4 mmol) was added. After several days, green crystals were obtained. Found: C, 38.58; H, 3.80; N, 8.67%. Calcd for $Mn_4C_{58}H_{68}N_{12}O_9(CF_3SO_3)_4 \cdot 2H_2O$: C, 38.60; H, 3.76; N, 8.71%. Iodometry of the complex revealed that the average oxidation state of manganese ions is 2.46, suggesting a (II,III) mixed valence state.

Figure 1 shows the molecular structure of the complex cation with selected bond distances and angles.[3)] The O5 of the complex lies on a crystallographic inversion center. Thus the complex consists of two crystallographically equivalent dinuclear units with alcholato and acetato bridges and those two dinuclear units are linked by oxide ion bridging Mn2 and Mn2'. Each manganese ion has a cis,trans-N_3O_3 donor set in a distorted octahedron. The average bond distances of Mn1-O and Mn1-N are 2.150 and 2.252 Å, respectively, and those of Mn2-O and Mn2-N 1.927 and 2.165 Å, respectively, indicating that the oxidation states of Mn1 and Mn2 are divalent and trivalent, respectively. Thus the complex is a firmly trapped mixed valence one. The Mn2-O-Mn2' is exactly linear and the Mn2-Mn2' distance is 3.554(2) Å. This is the first example which has an exactly linear Mn(III)-O-Mn(III) structure. Four pyridyl groups (A, B, C, and D rings in Fig. 1) coordinating to the Mn2 and Mn2' are almost parallel. Two pairs of pyridyl rings (A and C, and B and D) are faced each other and the distances between them are ≈3.7 Å, suggesting the presence of pairwise stacking interaction of pyridyl groups. This stacking interaction may contribute to the assembly of the two dinuclear units, resulting in a formation of the linear tetranuclear structure.

The effective magnetic moments at 300 and 80 K are 8.7 and 8.2 B.M./Mn_4, respectively. These values are substantially smaller than the expected value

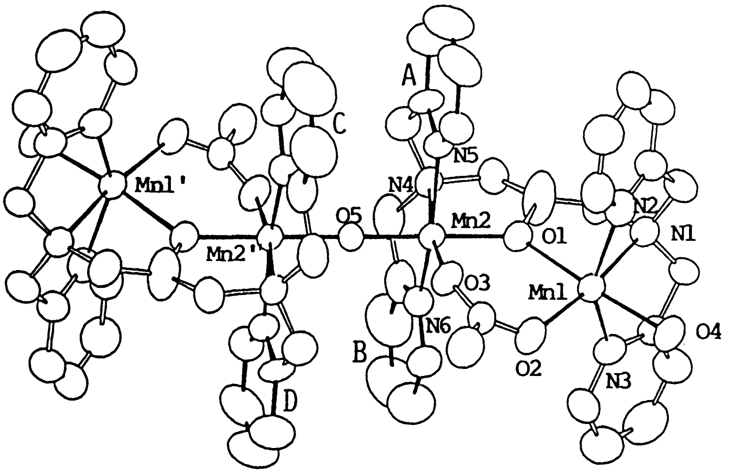


Fig. 1. Molecular stucture of $[Mn_4(tpdp)_2(CH_3COO)_2(O)(H_2O)_2]^{4+}$ cation, and selected bond distances (1/Å) and angles (ϕ/°): Mn1-Mn2 3.699(2), Mn2-Mn2' 3.554(2), Mn1-O1 2.168(7), Mn1-O2 2.083(9), Mn1-O4 2.199(8), Mn1-N1 2.274(9), Mn1-N2 2.243(9), Mn1-N3 2.239(9), Mn2-O1 1.912(7), Mn2-O3 2.091(8), Mn2-O5 1.777(2), Mn2-N4 2.215(9), Mn2-N5 2.148(9), Mn2-N6 2.132(10); Mn1-O1-Mn2 130.0(4), Mn2-O5-Mn2' 180.

(10.87 B.M.) for high spin Mn(II,III,III,II), indicative of the presence of an antiferromagnetic interaction between four manganese ions. The temperature dependence of the magnetic susceptibility from 80 - 300 K is shown in Fig. 2. A theoretical analysis using the pairwise isotropic spin exchange Hamiltonian $\mathcal{H} = -2\Sigma J_{ij} S_i \cdot S_j$ was not made because the eigenvalues can not be simply obtained by the usual vector coupling method. The effective magnetic moment implies that moderately strong antiferromagnetic interaction is present. Since the antiferromagnetic interactions in the dinuclear manganese(II,III) complexes with alcholato, phenolato, and/or carboxylato bridges have been shown to be weak ($-J < 10$ cm^{-1}),[4)] the antiferromagnetic interaction between manganese(II) and (III) ions through alcholato and acetato bridges in the present dinuclear mixed valence units seems to be also weak. Therefore we assumed that the antiferromagnetic interaction between the manganese(III) and (III) ions through the oxo bridge is much stronger than that between the manganese(II) and (III) ions. For preliminary analysis of the magnetic susceptibility data, we employed the following spin coupling model and spin Hamiltonian,

$$S_1 \overset{J_b}{\text{——}} (S_2 \overset{J_a}{\text{——}} S_3) \overset{J_b}{\text{——}} S_4 \quad (S_1 = S_4 = 5/2 \text{ and } S_2 = S_3 = 2)$$

$$\mathcal{H} = -2J_a S_2 \cdot S_3 - 2J_b S_1 \cdot (S_2 + S_3) - 2J_b S_4 \cdot (S_2 + S_3)$$

where $|J_a| \gg |J_b|$ and $(S_2 + S_3)$ couples with S_1 and S_4.

For fitting the data, g=2.0 was used, and the parameters J_a and J_b were varied. The data were well fitted with $J_a = -45$ cm^{-1} and $J_b = -6$ cm^{-1} as seen in Fig. 2, where solid lines are calculated curves. Thus the moderately strong antiferromagnetic interaction is present between the Mn(III) and Mn(III) ions through the oxo bridge, and the antiferromagnetic interactions between Mn(II) and Mn(III,III) unit through alcholato and acetato bridges are weak. For full analysis, low temperature data are necessary.

Since the absorption spectrum in acetonitrile was identical to the

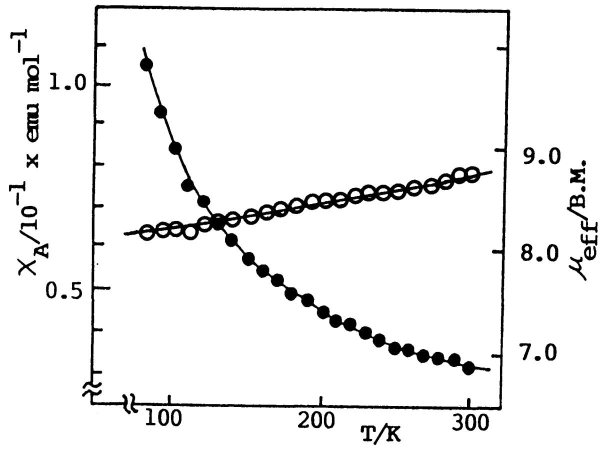


Fig. 2. Temperature dependence of the magnetic susceptibilities and the effective magnetic moments (μ_{eff}/Mn_4).

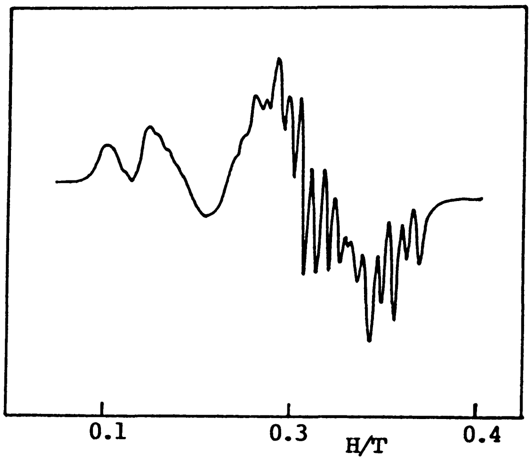


Fig. 3. ESR spectrum in Acetonitrile-ethanol-toluene (2 : 1 : 1) mixture at 12 K.

reflectance spectrum, the tetranuclear structure remained intact in acetonitrile. However, the complex readily decomposed in the presence of ethanol. ESR spectrum measured in acetonitrile-ethanol-toluene (2 : 1 : 1) solution at 12 K exhibits a signal with ^{55}Mn hyperfine structure (15 - 17 hyperfine lines extended over 2100 G range) at ≈ 3300 G (Fig. 3). Such multiline features have been observed in di-, tri-, and tetranuclear mixed valence complexes (Mn(II,III),[5)] Mn(III,IV),[6)] Mn(III,II,III),[4d)] and Mn(III,III,III,IV)[2d)]). The observed multiline signal at g≈2 seems to be attributable to a dinuclear mixed valence Mn(II,III) species formed by the decomposition of the tetranuclear complex judging from the width of resonance field of ^{55}Mn hyperfine lines.[5a)] Further studies are in progress to investigate the species responsible for this multiline spectrum.

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3) Crystal data: $[Mn_4(C_{27}H_{29}N_6O)_2(CH_3COO)_2(O)(H_2O)_2](CF_3SO_3)_4\cdot 2H_2O$: F.W=1929.31, monoclinic, $P2_1/c$, a=13.805(1), b= 21.095(3), c= 13.912(1) Å, β=99.883(6)°, V= 3991.4(8) $Å^3$, Z=2, Dm=1.60, Dc=1.61 g cm^{-3}, μ(Mo-Kα)=17.4 cm^{-1}. A total of 8716 reflections with $2\theta<55°$ were obtained, of which independent 2779 reflections with $|F_o|>3\sigma|F_o|$ were used for the structure determination. The current R factor is R=0.075.

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