Synthesis of a Tetranuclear Manganese Complex with a Cubane Core at the $\mathrm{Mn^{II}Mn^{III}Mn^{II}Mn^{III}}$ Oxidation Level

Masahiro Mikuriya,* Youichi Hashimoto, and Asako Kawamori†
Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662
†*Department of Physics, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662*

(Received September 1, 1995)

A novel tetranuclear manganese(II, III, II, III) complex with 2,6-bis[N-(4-imidazolylethyl)iminomethyl]-4-methylphenol (HL), $[\mathrm{Mn_4(L)_2(O)_2(CH_3COO)_2](ClO_4)_2 \cdot 2C_2H_5OH \cdot 2H_2O}$, has been synthesized and characterized by X-ray crystallography, infrared and electronic absorption spectroscopies, magnetic suscepitibility measurement, and ESR spectroscopy.

There has been considerable interest in the synthesis of dinuclear, trinuclear, and tetranuclear manganese complexes, since these molecules might be useful as model compounds for understanding the properties of the oxygen evolving center (OEC) of the photosystem II of green plants.[1] The arrangement of the manganese ions at any oxidation levels of the OEC is currently unclear. Brudvig, Dismukes, and Christou proposed $\mathrm{Mn_4O_4}$ cubanes to be involved in the OEC cycle, either at the higher or lower $\mathrm{S_n}$ states.[2] So far several cubane $\mathrm{Mn_4O_3X}$ (X = O, Cl, Br, F) complexes with bridging oxo, alkoxo, or halogeno ligands have been synthesized as models for the OEC.[3,4] However, their oxidation states have been confined only to $\mathrm{Mn^{II}_4}$ or $\mathrm{Mn^{III}_3Mn^{IV}}$ species and no other oxidation level has been found for cubane $\mathrm{Mn_4}$ complexes. We recently described the synthesis of dinuclear,[5-7] trinuclear,[8] and tetranuclear[6] manganese complexes which are formed by the use of some dinucleating ligands. In this study, we have isolated an interesting tetranuclear manganese complex with a cubane core at novel $\mathrm{Mn^{II}Mn^{III}Mn^{II}Mn^{III}}$ oxidation state by using a dinucleating ligand, 2,6-bis[N-(4-imidazolylethyl)iminomethyl]-4-methylphenol (HL). Herein we report the synthesis and structural characterization of the tetranuclear manganese complex, $[\mathrm{Mn_4(L)_2(O)_2(CH_3COO)_2](ClO_4)_2 \cdot 2C_2H_5OH \cdot 2H_2O}$ (**1**)

Complex **1** was prepared as follows. 2,6-Diformyl-4-methylphenol (32 mg) and histamine (44 mg) were dissolved in ethanol. Then manganese(II) acetate tetrahydrate (98 mg) and sodium perchlorate (98 mg) were successively added and the solution was filtered. To the filtrate was added 30 mg of triethylamine to give brown crystals of **1**. Its IR spectrum exhibits absorptions which confirmed the presense of coordinated C=N group of the dinucleating ligand L, bridging acetate group, and perchlorate ion [ν(C=N) 1631s $\mathrm{cm^{-1}}$, ν_{as}(COO) 1559s $\mathrm{cm^{-1}}$, ν_s(COO) 1407s $\mathrm{cm^{-1}}$, $\nu(\mathrm{ClO_4})$ 1142s, 1115s, 1084s $\mathrm{cm^{-1}}$]. The molecular structure of **1** was determined by X-ray crystallography.[9] A perspective view of the complex cation of **1** is shown in Figure 1. The complex has the crystallographic 2-fold axis passing through the centers of the cubane faces defined by Mnl, O2, Mnl', and O2' and by Mn2, O1, Mn2', and O1'. In one dinuclear unit, the Mnl and Mn2 atoms are bridged by a phenoxo-oxygen atom (O1) of the dinucleating ligand, oxo ion (O2), and one acetate ion. The Mnl atom has shorter equatorial [Mnl-O2, Mnl-O2', Mnl-O3 (1.897(8)—2.005(9) Å), and Mnl-N1 (2.072(17) Å] and long axial bond lengths [Mnl-O1 (2.240(12) Å) and Mnl-N2 (2.194(17) Å] indicative of Jahn-Teller distortion expected for a high-spin Mn(III) ion, while the bond lengths for the Mn2 atom [2.137(9)—2.281(8) Å] are typical of high-spin Mn(II) ion. The other dinuclear unit is related to this dinuclear unit by the 2-fold axis. It is noteworthy that the Mn-Mn separations span a much greater range [2.853(3)—3.520(4) Å] than those in the related cubane $\mathrm{Mn^{II}_4}$ [3.147(1)—3.45(1) Å][3] and $\mathrm{Mn^{III}_3Mn^{IV}}$ [2.786(3)—2.815(2), 3.195(1)—3.286(4) Å][4] complexes. To our knowledge, this is the first example of cubane structure in the manganese(II, III, II, III) mixed oxidation state. Model systems involving the present complex, which shows that a $\mathrm{Mn_4O_4}$ cubane structure exists in the $\mathrm{Mn_4}$(II, III, II, III) oxidation level, may be potentially of great value in contributing to the understanding of the photosynthetic process.

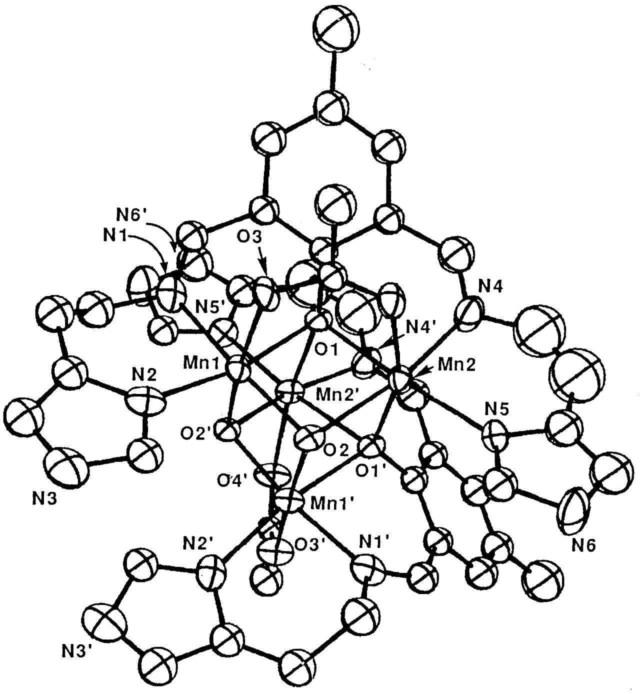

Figure 1. Perspective view of the complex cation of **1**. Selected interatomic distances (l/Å) and angles (ϕ/°): Mnl-Mnl' 2.853(3), Mnl-Mn2 3.037(4), Mnl-Mn2' 3.225(3), Mn2-Mn2' 3.520(4), Mnl-O1 2.240(12), Mnl-O2 1.909(12), Mnl-O2' 1.897(8), Mnl-O3 2.005(9), Mnl-N1 2.072(17), Mnl-N2 2.194(17), Mn2-O1 2.210(12), Mn2-O1' 2.281(8), Mn2-O2 2.139(12), Mn2-O4 2.137(9), Mn2-N4 2.150(17), Mn2-N5 2.175(16); Mnl-O1-Mn2 86.1(4), Mnl-O1-Mn2' 91.0(4), Mn2-O1-Mn2' 103.2(4), Mnl-O2-Mnl' 97.1(5), Mnl-O2-Mn2 97.0(5), Mnl'-O2-Mn2 105.9(5). Primes refer to the equivalent positions (1 - x, y, 3/2 - z).

The diffuse reflectance spectrum shows three absorption

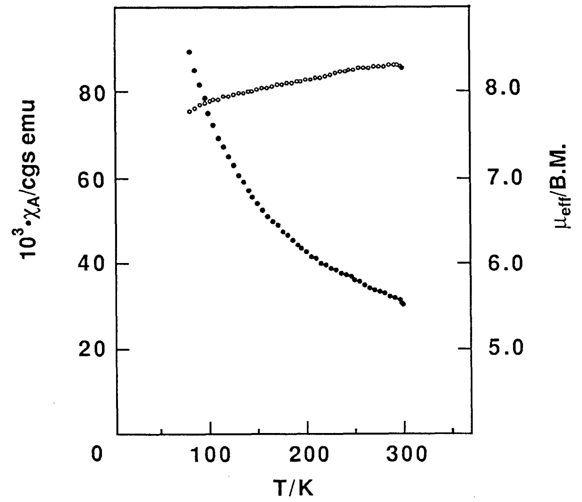

Figure 2. Magnetic susceptibility data of **1**.

bands at 378, 563 (shoulder), and 691 nm. This spectral feature is compatible with the $Mn^{II}Mn^{III}$ mixed-valence state.[7,10]

At 297 K the effective magnetic moment of **1** is 8.58 B.M. which is smaller than the expected one (10.86 B.M.) for four uncoupled spins ($S_{Mn1} = 2$, $S_{Mn2} = 5/2$, $S_{Mn1'} = 2$, and $S_{Mn2'} = 5/2$), and steadily decreases on decreasing temperature, reaching 7.56 B.M. at 80 K (Figure 2). This behavior indicates that there is significant antiferromagnetic coupling between the manganese ions.

As can be seen in Figure 3, the frozen solution ESR spectrum of **1** exhibits considerable manganese hyperfine structure. This spectrum is similar to those of analogous, structurally characterized $Mn^{II}Mn^{II}$ complexes which show Mn hyperfine multilines on $g \approx 2$ signal.[7] Complex **1** may break into two dinuclear units in DMF/toluene, giving rise to the multiline ESR signal.

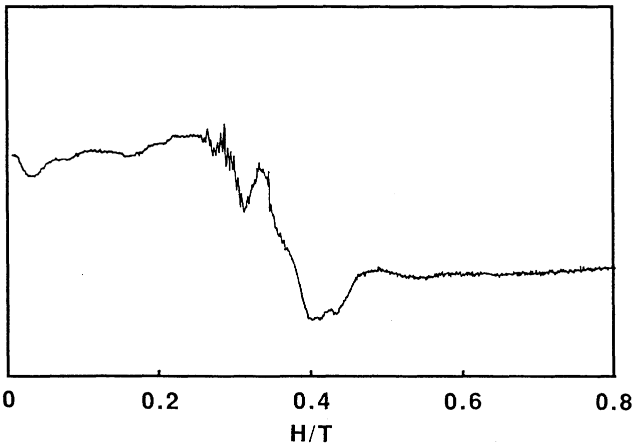

Figure 3. X-Band ESR spectrum of **1**, DMF/toluene glass at 80 K.

References and Notes

1 For examples, see G. W. Brudvig and R. H. Crabtree, *Prog. Inorg. Chem.*, **37**, 99 (1989); H. Kawasaki, M. Kusunoki, Y. Hayashi, M. Suzuki, K. Munezawa, M. Suenaga, H. Senda, and A. Uehara, *Bull. Chem. Soc. Jpn.*, **67**, 1310 (1994) and references therein.

2 G. W. Brudvig and R. H. Crabtree, *Proc. Natl. Acad. Sci. U.S.A.*, **83**, 4586 (1986); G. Christou and J. B. Vincent, *Biochim. Biophys. Acta*, **895**, 259 (1987); D. M. Proserpio, R. Hoffmann, and G. C. Dismukes, *J. Am. Chem. Soc.*, **114**, 4374 (1992).

3 S. Brooker, V. McKee, W. B. Shepard, and L. K. Pannell, *J. Chem. Soc., Dalton Trans.*, **1987**, 2555; K. L. Taft, A. Caneschi, L. E. Pence, C. D. Delfs, G. C. Papaefthymiou, and S. J. Lippard, *J. Am. Chem. Soc.*, **115**, 11753 (1993).

4 D. N. Hendrickson, G. Christou, E. A. Schmitt, E. Libby, J. S. Bashkin, S. Wang, H.-L. Tsai, J. B. Vincent, P. D. W. Boyd, J. C. Huffman, K. Folting, Q. Li, and W. E. Streib, *J. Am. Chem. Soc.*, **114**, 2455 (1992); M. W. Wemple, H.-L. Tsai, K. Folting, D. N. Hendrickson, and G. Christou, *Inorg. Chem.*, **32**, 2025 (1993); S. Wang, H.-L. Tsai, W. E. Streib, G. Christou, and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, **1992**, 1427; M. W. Wemple, D. M. Adams, K. Folting, D. N. Hendrickson, and G. Christou, *J. Am. Chem. Soc.*, **117**, 7275 (1995).

5 M. Mikuriya, K. Nakadera, and T. Tokii, *Inorg. Chim. Acta*, **194**, 129 (1992); M. Mikuriya, Y. Yamato, and T. Tokii, *Chem. Lett.*, **1992**, 1571; M. Mikuriya, Y. Yamato, and T. Tokii, *Bull. Chem. Soc., Jpn.*, **65**, 1466 (1992); M. Mikuriya and Y. Yamazaki, *Chem. Lett.*, **1995**, 373.

6 M. Mikuriya, Y. Yamato, and T. Tokii, *Bull. Chem. Soc., Jpn.*, **65**, 2624 (1992).

7 M. Mikuriya, T. Fujii, T. Tokii, and A. Kawamori, *Bull. Chem. Soc. Jpn.*, **66**, 1675 (1993).

8 M. Mikuriya, K. Majima, and Y. Yamato, *Chem. Lett.*, **1992**, 1929.

9 Crystal data for $[Mn_4(L)_2(O)_2(CH_3COO)_2](ClO_4)_2 \cdot 2C_2H_5OH \cdot 2H_2O$: $C_{46}H_{64}N_{12}O_{20}Cl_2Mn_4$, $M = 1395.7$, monoclinic, space group $C2/c$, $a = 17.161(6)$, $b = 19.887(6)$, $c = 19.933(6)$ Å, $\beta = 113.29(1)°$, $V = 6248(4)$ Å^3, $Z = 4$, $D_c = 1.48$ gcm^{-3}, $D_m = 1.51$ gcm^{-3}, μ(Mo-Kα) = 9.19 cm^{-1}, $F(000) = 2872$, $T = 293$ K. A total of 5356 reflections ($2 \le 2\theta \le 49°$) were measured on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation; 2225 with $I \ge 3\sigma(I)$ were assumed observed. The structure was solved by the direct methods and refined by the full-matrix least-squares method. Because of the paucity of the data, only the coordination environments (Mn, O, and N atoms) were refined anisotropically (number of parameters refined is 214). The refinement converged at $R = 0.107$, $R_w = 0.123$.

10 M. Suzuki, M. Mikuriya, S. Murata, A. Uehara, H. Oshio, S. Kida, and K. Saito, *Bull. Chem. Soc. Jpn.*, **60**, 4305 (1987).