CHEMISTRY LETTERS, pp. 923-926, 1990.

Synthesis and Characterization of a Novel Linear Tetranuclear Manganese Complex with Three Different Oxidation States (II,III,IV,II)

Masatatsu SUZUKI, Hitoshi SENDA,+ Machiko SUENAGA,
Toshiharu SUGISAWA, and Akira UEHARA*
Department of Chemistry, Faculty of Science, Kanazawa University,
Kanazawa 920
+Department of Chemistry, College of Liberal Arts,
Kanazawa University, Kanazawa 920

A novel linear tetranuclear manganese(II,III,IV,II) complex, was prepared, $[Mn_4(tpdp)_2(O)_2(H_2O)_4](ClO_4)_5\cdot4H_2O$, where Htpdp is 1,3-bis[bis(2-pyridylmethyl)amino]-2-propanol, and its crystal structure was determined by X-ray structure analysis. The complex cation consists of di(μ-oxo)dimanganese(III,IV) mixed valent unit to which two manganese(II) ions are linked by the alkoxo bridges of tpdp, forming a linear tetranuclear structure Mn(II,III,IV,II).

The oxygen-evolving center (OEC) in photosystem II in green plants and algae has been shown to contain four manganese ions (Mn_4 aggregate) which catalytically oxidize two water molecules to molecular oxygen. In the Kok's S state scheme,1) manganese ions have various oxidation states, II, III, and IV.2) Although the nature of the manganese center and the reaction mechanism of water oxidation remain ambiguous, the presence of di(μ-oxo)dimanganese unit has been suggested in the S_1 and S_2 states by ESR, EXAFS, and XANES studies.3) A variety of mixed valence tetranuclear complexes in various oxidation states have been devised as the models for S_n states in PS II.4) In this study, we report the synthesis of a novel linear tetranuclear manganese(II,III,IV,II) complex with di(μ-oxo)dimanganese(III,IV) unit, $[Mn_4(tpdp)_2(O)_2(H_2O)_4](ClO_4)_5\cdot4H_2O$ (**1**)5) and its structural characterization, where Htpdp is 1,3-bis[bis(2-pyridylmethyl)amino]-2-propanol. Previously we and Chan et al. have independently reported that tpdp forms another type of a linear tetranuclear manganese(II,III,-

III,II) complex, $[Mn_4(tpdp)_2(CH_3COO)_2(O)(H_2O)_2]^{4+}$ (**2**).$^{4f,4g)}$

The complex was prepared as follows: To a solution of Htpdp (1 mmol) in 20 cm^3 of ethanol was added $Mn(ClO_4)_2 \cdot 6H_2O$ (2 mmol) in 20 cm^3 of H_2O. Triethylamine (1 mmol) in 5 cm^3 of ethanol was added with stirring. The resulting solution gradually reacted with O_2 to change in color from original pale yellow to brown. The brown solution was allowed to stand overnight to give brown crystals. Recrystallization was achieved from hot water. Found: C, 35.98; H, 4.03; N, 9.41%. Calcd for $Mn_4C_{54}H_{66}N_{12}O_8$-$(ClO_4)_5 \cdot 4H_2O$: C, 36.03; H, 4.14; N, 9.34%. The complex was also prepared by recrystallizing the perchlorate salt of **2** from hot water under O_2.

The average oxidation state of the four manganese ions determined by the method of Blecher and West$^{6)}$ was 2.75, indicating that a possible combination of the oxidation states of four manganese ions is either (Mn^{2+}, $3Mn^{3+}$) or ($2Mn^{2+}$, Mn^{3+}, Mn^{4+}). The replacement of Mn^{2+} ion with Zn^{2+} ion was attempted in order to clarify the oxidation states of four manganese ions. The reaction of **1** with Zn^{2+} ion in water resulted in the replacement of Mn^{2+} ion by Zn^{2+} ion to give a dark brown heterometal complex, $[Zn_2Mn_2(tpdp)_2(O)_2(H_2O)_4](ClO_4)_5 \cdot 1.5H_2O$ (**3**).$^{7)}$ The comparisons of ESR and cyclic voltamograms of **1** and **3** strongly suggested the presence of Mn_2(III,IV) unit (vide infra).

A dark brown prismatic crystal with dimensions of 0.1 x 0.2 x 0.2 mm^3 was used for X-ray structure analysis. Crystal data: $[Mn_4(tpdp)_2(O)_2(H_2O)_4](ClO_4)_5 \cdot 4H_2O$: F.W= 1800.26, monoclinic, $C2/c$,$^{8)}$ a= 23.664(9), b=21.748(10), c= 16.319(8) Å, β=118.96(3)°, V= 7348.8(59) $Å^3$, Z=4, Dm=1.63, Dc= 1.63 g cm^3, μ(Mo-Kα)=9.89 cm^{-1}. Intensity data were collected by a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromated Mo-Kα radiation. A total of 8074 reflections with 2θ < 55° were obtained, of which independent 2424 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 current R factor is 0.064.

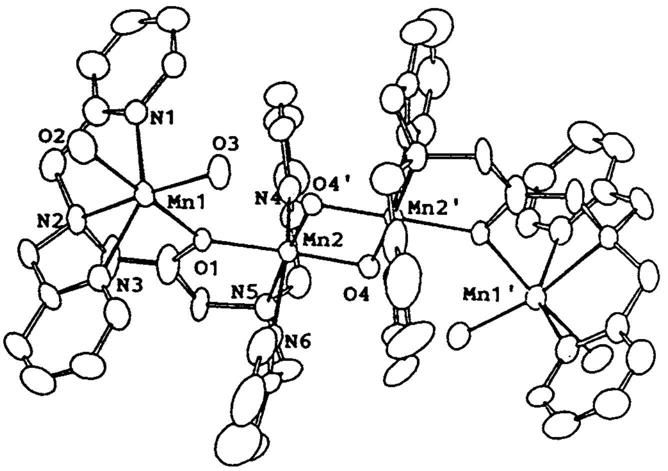

Fig. 1. Selected bond distances (l/Å) and angles (ϕ/°): Mn1-Mn2 3.814(3), Mn2-Mn2' 2.727(2), Mn1-O1 2.189(6), Mn1-O2 2.239(8), Mn1-O3 2.091(4), Mn1-N1 2.214(9), Mn1-N2 2.308(4), Mn1-N3 2.232(8), Mn2-O1 1.945(7), Mn2-O4 1.838(7), Mn2-O4' 1.789(2), Mn2-N4 2.124(9), Mn2-N5 2.090(3), Mn2-N6 2.182(9); Mn1-O1-Mn2 134.6(7), Mn2-O4(O4')-Mn2' 97.5(3).

The crystal structure consists

of a tetranuclear complex cation, five perchlorate anions, and four water molecules. One of the five perchlorate anions is disordered at two positions with occupancy factor 0.5 around two hold axis. Figure 1 shows the molecular structure of the complex cation. Since the complex cation possesses C_2 symmetry, Mn1 and Mn1' are crystallographically equivalent, and Mn2 and Mn2' also equivalent. All the manganese ions are in distorted octahedron. The complex cation consits of di(μ-oxo)dimanganese unit to which additional two manganese atoms are linked by the alkoxo bridges of tpdp, forming a linear tetranuclear structure. The average bond distances of Mn1-N and Mn1-O are 2.25 and 2.17 Å, respectively, which are consistent with those of Mn^{2+} moiety in **2**. The Mn2-N bond distances range from 2.09 to 2.18 Å, which are slightly shorter than those of Mn^{3+} moiety of **2**, and are comparable to the mean value of Mn(III)-N and Mn(IV)-N bond distances in the dinuclear manganese(III,IV) complex with N_3O donor set, $[Mn_2(N_3O\text{-}py)_2(O)_2]^+$ (**4**) (HN_3O-py=bis(2-pyridylmethyl)(carboxymethyl)amine).[9] The average Mn-O(oxo) bond distance (1.81 Å) is also comparable to the mean value of the Mn(III)-O(oxo) and Mn(IV)-O(oxo) distances in **4**. For the equivalence of Mn2 and Mn2', there are two possible cases: (1) The Mn2 and Mn2' moieties are chemically equivalent, corresponding to Mn^{2+}-$Mn^{3.5+}$-$Mn^{3.5+}$-Mn^{2+} arrangement, i.e., the seventh Mn d electron is delocalized completely between Mn2 and Mn2' moieties. (2) The Mn2 and Mn2' moieties are not chemically equivalent and the observed structure is a superposition of Mn^{2+}-Mn^{3+}-Mn^{4+}-Mn^{2+} and Mn^{2+}-Mn^{4+}-Mn^{3+}-Mn^{2+} arrangements (disordered structure). The latter structure (Mn^{2+}-Mn^{3+}-Mn^{4+}-Mn^{2+} arrangement) is strongly suggested by the following ESR spectrum of **3**.

The ESR spectrum of **1** shows broad signal. The replacement of Mn^{2+} ions by diamagnetic Zn^{2+} ions causes a dramatic change in the ESR spectrum: the spectrum of **3** exhibits a sixteen ^{55}Mn hyperfine pattern at $g \approx 2$ extended over 1200 G (Fig. 2). This is characteristic of those of the antiferromagnetically coupled dinuclear Mn_2(III,IV) complexes,[10] indicating the presence of di(μ-oxo)dimanganese(III,IV) unit and the valences of manganese ions are firmly trapped.

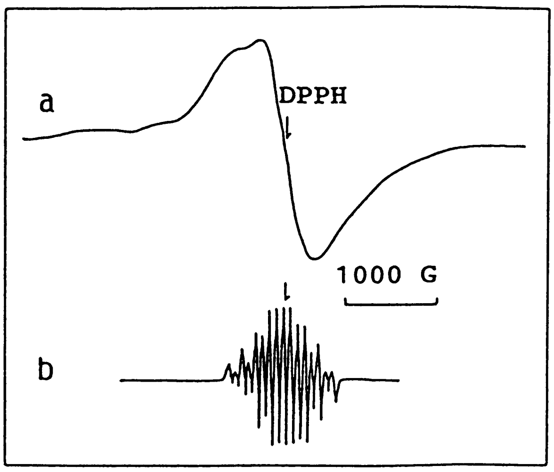

Fig. 2. ESR spectra of **1** (**a**) and **3** (**b**) in acetonitrile-toluene-ethanol (2 : 1 : 1) at 77 K.

The cyclic voltamograms of **1** and **3** show two quasi-reversible redox couples at 0.39 and 0.93 V vs. SCE, and 0.50 and 0.96 V vs. SCE, respectively, in acetonitrile containing 0.1 mol dm^3 $(n\text{-butyl})_4NClO_4$. The similarity of the cyclic voltamograms of **1** and **3** indicates that these two redox couples are due to Mn_2(III,IV) moiety, but not Mn(II) moiety. The reduction at 0.0 V and oxidation at 1.0 V vs. SCE of **1** reveal that the redox couples at 0.39 and 0.93 V vs. SCE correspond to one electron transfer assignable to Mn_2(III,IV)/Mn_2(III,III) and Mn_2(IV,IV)/Mn_2(III,IV) couples, respectively.

The effective magnetic moment of **1** is almost constant from 8.2 B.M./Mn_4 at 300 K to 8.1 B.M./Mn_4 at 80 K which are smaller than the spin-only value (10.44 B.M.) of Mn_4(II,III,IV,II), indicating the presence of antiferromagnetic interaction between four manganese ions. Detailed magnetic study of these complexes will be reported elsewhere.

The present study was partially supported by a Grant-in-Aid for Scientific Recearch No. 01540506 from Ministry of Education, Science, and Culture.

References

1) B. Kok, B, Forbush, and M. McGloin, Photochem. Photobiol., 11, 457 (1970).
2) K. Sauer, Acc. Chem. Res., 13, 249(1980); G. W. Brudvig and R. H. Crabtree, Proc. Natl. Acad. Sci. U.S.A., 83, 4586(1986); G. C. Dismukes, Photochem. Photobiol., 43, 99(1986).
3) G. C. Dismukes, K. Ferris, and P. Watnick, Photobiochem. Photobiophys., 3, 234(1982); J. C. Paula, W. F. Beck, and G. W. Brudvig, J. Am. Chem. Soc., 108, 4002(1986); V. K. Yachandra, R. D. Guiles, A. F. Mcdermott, J. L. Cole, R. D. Britt, S. L. Dexheimer, K. Sauer, and M. P. Klein, Biochemistry, 26, 5974(1987); M. Kusunoki, T. Ono, T. Matsushita, H. Oyanagi, and Y. Inoue, private communication.
4) a) K. Wieghardt, U. Bossek, and W. Gebert, Angew. Chem., Int. Ed. Engle., 22, 328(1983); b) J. S. Bashkin, H. R. Chang, W. E. Streib, J. C. Huffman, D. N. Hendrickson, and G. Christou, J. Am. Chem. Soc., 109, 6502(1987); c) K. Wieghardt, U. Bossek, B. Nuber, J. Weiss, J. Bonvoisin, M. Corbella, S. E. Vitols, and J. J. Girerd, ibid., 110, 7398(1988); d) K. S. Hagen, T. D. Westmoreland, M. J. Scott, and W. H. Armstrong, ibid., 111, 1907(1989); e) J. B. Vincent, C. Christmas, H. R. Chang, Q. Li, P. D. W. Boyd, J. C. Huffman, D. N. Hendrickson, and G. Christou, ibid., 111, 2086(1989); f) M. Suzuki, T. Sugisawa, H. Senda, H. Oshio, and A. Uehara, Chem. Lett., 1989, 1091; g) M. K. Chan and W. H. Armstrong, J. Am. Chem. Soc., 111, 9121(1989).
5) Triflate salt of Compound **1** has been reported by Chan and Armstrong. Their assignment of the oxidation states of four manganese ions are (II,III,III,III): M. K. Chan and W. H. Armstrong, Book of Abstracts, The 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawai, Dec. 17 - 22, 1989, and accompaning poster presentation.
6) R. Blecher and T. S. West, Anal. Chim. Acta, 6, 322(1952).
7) Found: C, 36.02; H, 3.59; N, 9.67; Mn, 6.16%. Calcd for $Mn_2Zn_2C_{54}H_{66}N_{12}O_8(ClO_4)_5 \cdot 1.5H_2O$: C, 36.52; H, 3.92; N, 9.46; Mn, 6.19%.
8) There are two possible choices of space groups; $C_{2/c}$ and C_c. The former was selected, because the results obtained by assuming C_c space group were very poor.
9) M. Suzuki, H. Senda, Y. Kobayashi, H. Oshio, and A. Uehara, Chem. Lett., 1988, 1763.
10) For example, S. R. Cooper, G. C. Dismukes, M. P. Klein, and M. Calvin, J. Am. Chem. Soc., 100, 7248(1978).

(Received April 2, 1990)