

Dinuclear Manganese(III,IV) and Manganese(IV,IV) Complexes  
with Tris(2-pyridylmethyl)amine

Masatatsu SUZUKI, Seiji TOKURA, Masahiko SUHARA,  
and Akira UEHARA\*

Department of Chemistry, Faculty of Science, Kanazawa University,  
Kanazawa 920

Dinuclear manganese(III,IV) and (IV,IV) complexes,  $[\text{Mn}_2(\text{N}_4\text{-py})_2(\text{O})_2](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$  (**1**) and  $[\text{Mn}_2(\text{N}_4\text{-py})_2(\text{O})_2](\text{ClO}_4)_4 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$  (**2**), were prepared, where  $\text{N}_4\text{-py}$  represents tris(2-pyridylmethyl)amine. Both complexes **1** and **2** exhibited strong anti-ferromagnetic interaction with  $J \approx -159$  and  $-137 \text{ cm}^{-1}$ , respectively. ESR spectrum of **1** showed a sixteen  $^{55}\text{Mn}$  hyperfine pattern at  $g=2$ , which is indicative of a Mn(III,IV) trapped valence state.

Dinuclear or tetranuclear manganese site involved in photosystem II in green plants has been known to play an essential role in the oxidation of water to molecular oxygen.<sup>1)</sup> Although details of structure of the manganese site and reaction mechanism associated with water oxidation are still ambiguous, manganese ions undergo higher oxidation states in the catalytic cycle. Dinuclear and tetranuclear manganese complexes in higher oxidation states such as three and four are important as model compounds for the manganese site in PS II. However, there have been reported only a limited number of dinuclear manganese(III,IV)<sup>2-4)</sup> and (IV,IV)<sup>5)</sup> complexes, especially only one example has been known for the isolation of both manganese(III,IV) and (IV,IV) complexes with the same ligand system.<sup>2a,5a)</sup>

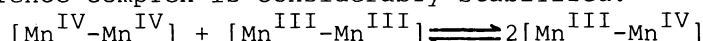
In this communication, we report the syntheses and some physicochemical properties of dinuclear manganese(III,IV) and (IV,IV) complexes with two oxo bridges,  $[\text{Mn}_2(\text{N}_4\text{-py})_2(\text{O})_2](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$  (**1**) and  $[\text{Mn}_2(\text{N}_4\text{-py})_2(\text{O})_2](\text{ClO}_4)_4 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$  (**2**), where  $\text{N}_4\text{-py}$  is tris(2-pyridylmethyl)amine.

Complex **1** was prepared as follows: To a solution of  $\text{N}_4\text{-py}$  (1 mmol) and  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1 mmol) in  $20 \text{ cm}^3$  of  $\text{H}_2\text{O}$  was added several drops of 35%  $\text{H}_2\text{O}_2$ . The pH of the solution was adjusted to ca. 8 by adding an aqueous solution of  $\text{NaHCO}_3$ . The resulting dark green solution was left to stand overnight to give dark green crystals. Recrystallization was carried out from hot water. Found: C, 41.64; H, 3.49; N, 10.59%. Calcd for  $\text{C}_{36}\text{H}_{36}\text{N}_8\text{O}_2(\text{ClO}_4)_3\text{Mn}_2 \cdot \text{H}_2\text{O}$ : C, 41.62; H, 3.69; N, 10.79%.

Complex **2** was obtained by electrochemical oxidation of **1** in acetonitrile at 1.20 V vs. SCE. During the oxidation green powder was precipitated out. Found: C, 38.85; H, 3.68; N, 10.65%. Calcd for  $\text{C}_{36}\text{H}_{36}\text{N}_8\text{O}_2(\text{ClO}_4)_4\text{Mn}_2 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ : C, 38.70; H, 3.50; N, 10.69%.

The average oxidation state of manganese ions in 1 was determined by the redox titration: manganese(III) and (IV) ions were reduced to manganese(II) by the reaction of a calculated amount of excess oxalic acid and then the amount of remaining oxalic acid was titrated by a potassium permanganate standard solution. The result thus obtained proved that the average oxidation state of the manganese ions is 3.5 (the experimental value=3.4). The molar conductivities of 1 and 2 in acetonitrile are 406 and 501  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , indicative of a 3 : 1 electrolyte and a 4 : 1 one, respectively. On the basis of the average oxidation state of manganese ions, and the molar conductivity data as well as electrochemical and magnetic properties (vide infra), it is concluded that complexes 1 and 2 are formulated as  $[\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}(\text{N}_4\text{-py})_2(\text{O})_2](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$  and  $[\text{Mn}_2^{\text{IV}}(\text{N}_4\text{-py})_2(\text{O})_2](\text{ClO}_4)_4 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ , respectively, where two manganese ions are linked by two oxo bridges as was found in  $[\text{Mn}_2(\text{phen})_4(\text{O})_2]^{3+}$  or  $4+$  (phen=1,10-phenanthroline).<sup>2c)</sup> The presence of acetonitrile in 2 was confirmed by the appearance of the  $\nu(\text{CN})$  of  $\text{CH}_3\text{CN}$  at  $2240 \text{ cm}^{-1}$  in the IR spectrum.

Figure 1 shows a cyclic voltammogram of 1 in acetonitrile containing ca.  $0.1 \text{ mol dm}^{-3}$   $(\text{n-C}_4\text{H}_9)_4\text{NClO}_4$  at glassy carbon electrode by using an SCE as reference electrode. The complex exhibits two sets of reversible redox waves at 0.24 ( $E_{1/2}^a$ ) and 1.04 ( $E_{1/2}^b$ ) V vs. SCE. Controlled potential electrolysis of 1 was carried out in order to determine the numbers ( $n$ ) of electron transferred in the above two processes. The reduction at 0.00 V and the oxidation at 1.20 V (vs. SCE) gave the  $n$  value of  $0.97 \pm 0.02$ . Thus the above two redox couples correspond to the redox reactions of  $\text{Mn}(\text{III,IV})/\text{Mn}(\text{III,III})$  and  $\text{Mn}(\text{IV,IV})/\text{Mn}(\text{III,IV})$ , respectively. From the separation of  $E_{1/2}^a$  and  $E_{1/2}^b$ , comproportionation constant ( $K$  at  $20^\circ \text{C}$ ) of the following reaction is calculated to be  $5.8 \times 10^{13}$ , indicating that the mixed valence complex is considerably stabilized.



The magnetic moments ( $\mu_{\text{eff}}/\text{Mn}_2$ ) of 1 and 2 varied from 2.33 and 2.23 B.M. at 300 K to 1.79 and 0.66 B.M. at 80 K, respectively. Figure 2 shows temperature dependences of the magnetic susceptibilities of 1 and 2 over the temperature range 80 - 300 K. The results were analyzed by an isotropic spin-spin exchange interaction model ( $M = -2JS_1 \cdot S_2$ ). The experimental values were well interpreted in terms of the following parameters:  $J = -159 \text{ cm}^{-1}$ ,  $\text{TIP} = 100 \times 10^{-6} \text{ emu mol}^{-1}$ , impurity=0.3% as monomeric manganese(III) complex for 1;  $J = -137 \text{ cm}^{-1}$ ,  $\text{TIP} = 100 \times 10^{-6} \text{ emu mol}^{-1}$ , impurity=0.25% as monomeric manganese(III) complex for 2, where  $g = 2.00$  was used for fitting. Thus both complexes exhibit strong antiferromagnetic interaction between  $\text{Mn}(\text{III})$  and (IV), and  $\text{Mn}(\text{IV})$  and (IV) ions, respectively. These values are comparable to

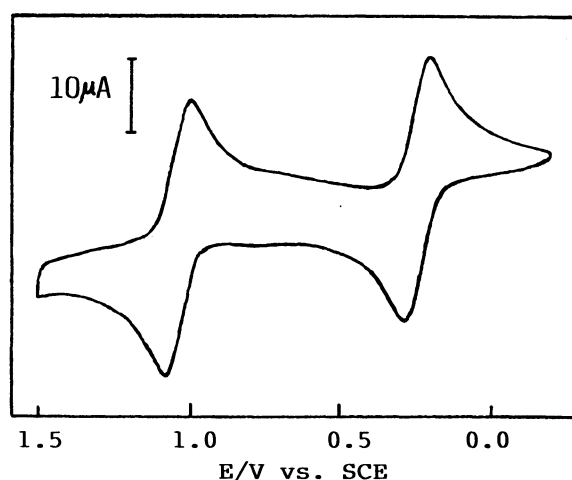


Fig. 1. Cyclic voltammogram of 1 in acetonitrile. The scan rate is  $100 \text{ mV s}^{-1}$ .

those of  $[\text{Mn}_2(\text{phen})_4(\text{O})_2]^{3+}$  ( $J = -134 - -150 \text{ cm}^{-1}$ ) and  $[\text{Mn}_2(\text{phen})_4(\text{O})_2]^{4+}$  ( $J = -144 \text{ cm}^{-1}$ ),<sup>2b,c)</sup> indicating that the structures of the present complexes are similar to those of the above phen complexes.

The frozen solution ESR spectrum of 1 exhibits a sixteen  $^{55}\text{Mn}$  hyperfine pattern at  $g=2$  at 77 K (Fig. 3a). The spectrum showed no appreciable change in shape upto 200 K. Such a sixteen hyperfine pattern at  $g=2$  is expected for an anti-ferromagnetically coupled Mn(III,IV) dimer with a spin state of  $S=1/2$  where two manganese ions are inequivalent. A simulation of the spectrum was carried out by using the following spin Hamiltonian,

$$\mathcal{H} = g_z \beta H_z S_z + g_{xy} \beta (H_x S_x + H_y S_y) + A_{z1} S_z I_{z1} + A_{xy1} (S_x I_{x1} + S_y I_{y1}) + A_{z2} S_z I_{z2} + A_{xy2} (S_x I_{x2} + S_y I_{y2})$$

A preliminarily simulated spectrum is given in Fig. 3b. The resonance fields are almost reproduced by using the parameters ( $g_z = g_{xy} = 2.002$ ,  $A_{z1} = A_{xy1} = 151 \text{ G}$ , and  $A_{z2} = A_{xy2} = 75 \text{ G}$ ). Introduction of small anisotropies in  $g$  ( $2.002 - 2.007$ ) and  $A$  (a few gauss) tensors caused no significant change in spectrum. Little anisotropy in  $g$  and  $A$  tensors implies that the structures of two manganese moieties are close to the regular octahedron. ESR results indicate that the complex is in a firmly trapped mixed valence state.

Complex 1 showed absorption bands in acetonitrile in the visible region at  $15200 \text{ cm}^{-1}$  ( $\epsilon = 620 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ ),  $17830 \text{ cm}^{-1}$  ( $\epsilon = 760 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ ), and  $22570 \text{ cm}^{-1}$  ( $\epsilon = 1490 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ ), which resemble those of  $[\text{Mn}_2(\text{phen})_4(\text{O})_2]^{3+}$  except for the absence of intervalence band (IT) at ca.  $12000 \text{ cm}^{-1}$ .<sup>2a)</sup> The absence of IT band in the present complex suggests that degree of electron delocalization is smaller than that in the phen complex. The absorption spectrum of 2 in acetonitrile showed several bands in the visible and near infrared regions, which is quite different from that of  $[\text{Mn}_2(\text{phen})_4(\text{O})_2]^{4+}$  that has no absorption bands in the visible region.<sup>2a)</sup> The absorption bands of 2 were located at  $11800 \text{ cm}^{-1}$  (shoulder:

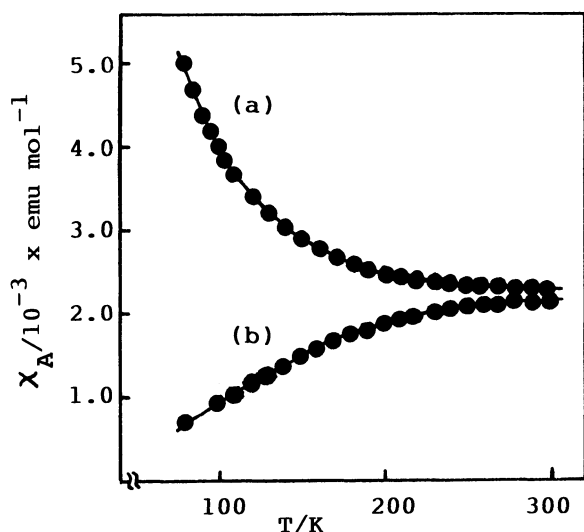


Fig. 2. Temperature dependence of magnetic susceptibilities of 1 (a) and 2 (b).

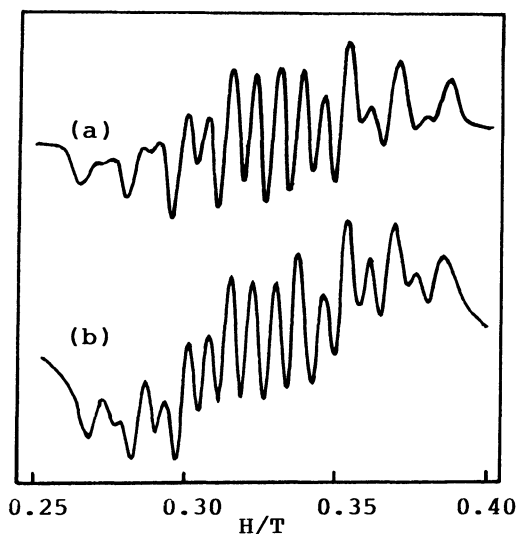


Fig. 3. ESR spectrum of 1 in acetonitrile at 77 K (a) and a simulated one (b) obtained with the parameters described in the text.

$\epsilon \approx 200 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ ),  $12500 \text{ cm}^{-1}$  (shoulder:  $\epsilon \approx 240 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ ),  $15600 \text{ cm}^{-1}$  ( $\epsilon \approx 1100 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ ),  $16700 \text{ cm}^{-1}$  (shoulder;  $\epsilon \approx 900 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ ),  $18800 \text{ cm}^{-1}$  ( $\epsilon \approx 1000 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ ),  $21700 \text{ cm}^{-1}$  (shoulder:  $\epsilon \approx 3100 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ ), and  $23990 \text{ cm}^{-1}$  ( $\epsilon \approx 5000 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ ).<sup>6)</sup> Mn(IV) is isoelectronic with Cr(III) and expected to show two d-d bands ( ${}^4A_{2g} \longrightarrow {}^4T_{2g}$  and  ${}^4T_{1g}$  in Oh symmetry) at higher energy than Cr(III) complexes. The band at  $15600 \text{ cm}^{-1}$  may not be attributable to the d-d transitions because of its high intensity and low transition energy. We tentatively assigned the bands to charge transfer transitions from bridging oxo groups to  $d\pi^*$  orbitals of Mn(IV) ions. The bands at higher energy than  $15600 \text{ cm}^{-1}$  are probably ascribed not only to the d-d transitions but also charge transfer transitions from bridging oxo and/or pyridyl groups to  $d\pi^*$  and/or  $ds^*$  orbitals of Mn(IV). The bands at  $11800$  and  $12500 \text{ cm}^{-1}$  are tentatively assigned to the spin forbidden transitions ( ${}^4A_{2g} \longrightarrow {}^2T_{1g}$  and/or  ${}^2E_g$ ). Although the intensity of the spin forbidden transition is generally very small, such intensity enhancement ( $\epsilon \approx 200 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ ) may be interpreted in terms of cooperative effect in the dinuclear unit which was also observed in dinuclear high spin iron(III,III) complexes.<sup>7)</sup>

Recently Ramarai et al. reported that  $[\text{Mn}_2(\text{phen or bpy})_4(\text{O})_2]^{3+}$  oxidized  $\text{H}_2\text{O}$  to  $\text{O}_2$  in the presence of Ce(IV) ions.<sup>8)</sup> The present complex, however, did not show such oxidation in similar conditions.

The present work was supported by a Grant-in-Aid for Scientific Research No. 62540458 from Ministry of Education, Science, and Culture.

#### References

- 1) K. Sauer, *Acc. Chem. Res.*, **13**, 249(1980); J. C. de Paula, W. F. Beck, and G. W. Brudvig, *J. Am. Chem. Soc.*, **108**, 4002(1986).
- 2) a) S. R. Cooper and M. Calvin, *J. Am. Chem. Soc.*, **99**, 6623(1977); b) S. R. Cooper, G. C. Dismukes, M. P. Klein, and M. Calvin, *ibid.*, **100**, 7248(1978); c) M. Stebler, A. Ludi, and H. B. Bürgi, *Inorg. Chem.*, **25**, 4743(1986).
- 3) K. Wieghardt, U. Bossek, J. Bonvoisin, P. Beauvillan, J. J. Girerd, B. Nuber, J. Weiss, and J. Heinze, *Angew. Chem., Int. Ed. Engl.*, **25**, 1030(1986); K. Wieghardt, U. Bossek, L. Zsolnai, G. Hutter, G. Blondin, J. J. Girerd, and F. Babonneau, *J. Chem. Soc., Chem. Commun.*, **1987**, 651.
- 4) M. A. Collins, D. J. Hodgson, K. Michelsen, and K. Towle, *J. Chem. Soc., Chem. Commun.*, **1987**, 1659.
- 5) a) H. A. Goodwin and R. N. Sylva, *Aust. J. Chem.*, **20**, 629(1967); b) Y. Yoshino, I. Taminaga, M. Kokiso, and T. Uehiro, *Bull. Chem. Soc. Jpn.*, **47**, 2787(1974).
- 6) Since the complex decomposed in acetonitrile with time, the spectrum was measured just after dissolved, which was in good agreement with the reflectance spectrum.
- 7) J. S. Loehr, T. M. Loehr, A. G. Mauk, and H. B. Gray, *J. Am. Chem. Soc.*, **102**, 6992(1980).
- 8) R. Ramarai, A. Kira, and M. Kaneko, *Angew. Chem., Int. Ed. Engl.*, **25**, 825(1986).

(Received December 21, 1987)