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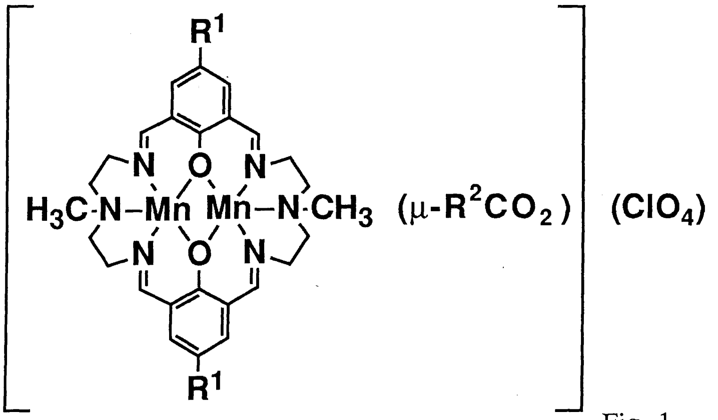
Synthesis and Electrochemical Properties of Dinuclear Manganese(II) Complexes with Octadentate Schiff-base Macrocycles. Fine Tuning of the Redox Behavior

Yoshiya IKAWA, Toshi NAGATA,* and Kazuhiro MARUYAMA
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

A series of dinuclear manganese(II) complexes $[R^1\text{-LMn}_2(R^2CO_2)]ClO_4$ were synthesized and X-ray crystal structure analysis of $[CH_3\text{-LMn}_2(CH_3CO_2)]ClO_4$ (**1**) was performed. Two manganese ions of **1** were six-coordinate with highly deformed octahedral structure. Electrochemical measurements of these complexes revealed that both the substituents of the phenol ring and those on the ligating acetate effectively control the redox properties of the Mn(II) center.

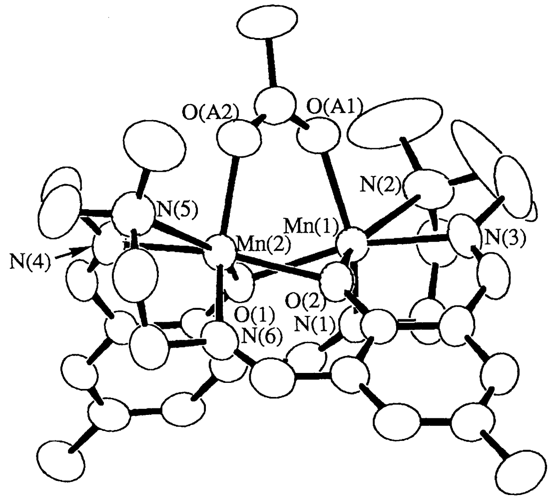
It is well recognized that manganese ion plays important roles in many biological processes.[1] Especially Mn catalase has a dinuclear manganese core as its active site,[2] and PS II reaction center of cyanobacteria and green plants contain a tetranuclear cluster as the active site of oxygen evolving complexes.[3] Recently a lot of dinuclear and multinuclear manganese complexes have been synthesized as models of these manganese redox enzymes.[4] However, only a few examples were reported in which the redox properties of the Mn centers could be controlled systematically. We wish to report here the synthesis and redox properties of a series of dinuclear manganese(II) complexes $[R^1\text{-LMn}_2(R^2CO_2)]ClO_4$, where R^1-L is an octadentate (N_6O_2) Schiff-base macrocyclic ligand and R^2CO_2 is a substituted acetate ion. It was found that the introduction of various substituents at R^1 and/or R^2 resulted in significant changes in the redox behavior of these complexes.

A series of complexes $[R^1\text{-LMn}_2(R^2CO_2)]ClO_4$ were prepared by the reaction of 4-substituted 2,6-diformylphenol (3.05 mmol), bis(2-aminoethyl)methylamine (3.05 mmol) and $Mn(ClO_4)_2\cdot 6H_2O$ (3.05 mmol) in the presence of R^2CO_2Na (7.10 mmol) in MeOH (40 ml).[5] Synthesized dinuclear Mn(II) complexes are summarized in Fig. 1. In all cases desired dinuclear Mn(II) complexes were obtained as yellow solids.



1: $R^1 = CH_3$, $R^2 = CH_3$
2: $R^1 = CH_3$, $R^2 = ClCH_2$
3: $R^1 = CH_3$, $R^2 = Cl_2CH$
4: $R^1 = CH_3$, $R^2 = Cl_3C$
5: $R^1 = CH_3$, $R^2 = F_3C$
6: $R^1 = OCH_3$, $R^2 = CH_3$
7: $R^1 = H$, $R^2 = CH_3$
8: $R^1 = F$, $R^2 = CH_3$
9: $R^1 = Br$, $R^2 = CH_3$
10: $R^1 = Br$, $R^2 = F_3C$

Fig. 1.



Distances (Å)			
Mn(1)-O(1)	2.189(4)	Mn(2)-O(1)	2.197(4)
Mn(1)-O(2)	2.181(4)	Mn(2)-O(2)	2.178(4)
Mn(1)-N(1)	2.189(5)	Mn(2)-N(4)	2.206(5)
Mn(1)-N(2)	2.493(6)	Mn(2)-N(5)	2.558(5)
Mn(1)-N(3)	2.202(5)	Mn(2)-N(6)	2.191(5)
Mn(1)-O(A1)	2.088(4)	Mn(2)-N(6)	2.191(5)
Mn(1)-Mn(2)	3.239(1)		
Angles (deg)			
O(1)-Mn(1)-O(2)	74.9(1)	O(1)-Mn(2)-O(2)	74.8(1)
N(1)-Mn(1)-O(A1)	137.4(2)	N(6)-Mn(2)-O(A2)	141.9(2)
Mn(1)-O(1)-Mn(2)	95.2(1)	Mn(1)-O(2)-Mn(2)	96.0(2)

Fig. 2. ORTEP view of **1** and selected bond distances and angles.

Single crystals of **1**·DMF suitable for X-ray analysis were obtained by vapor diffusion of Et_2O into a DMF solution of **1**. The molecular structure of **1** is shown in Fig. 2.⁶⁾ The macrocycle serves as an octadentate ligand, and an acetate anion binds in a bridging manner. Each Mn ion is coordinated by two bridging phenolic oxygens, three nitrogens and one acetate oxygen. The whole coordination geometry around each Mn ion is roughly octahedral but severely deformed. The distances Mn(1)-N(2) and Mn(2)-N(5) are much longer than the other Mn-N distances. The bond angles around each Mn are also quite deviated from the ideal values. In contrast to the previously reported dinuclear Mn(II) complexes with Schiff-base macrocycles,⁷⁾ the phenolic oxygens and the imino nitrogens are not coplanar; two imino nitrogens (N(1) and N(6)) coordinate axially (i.e. trans to the acetate-O) and the tertiary amino nitrogens (N(2) and N(5)) occupy the equatrial sites.

Although X-ray structures of complexes **2-10** are not available at present, we assume they have very similar structures to that of **1**. Elemental analysis and IR spectra of **1-10** were consistent with the composition $[R^1\text{-}LMn_2(R^2CO_2)]ClO_4$. FAB-MS spectra showed a strong peak corresponding to $[R^1\text{-}LMn_2(R^2CO_2)]^+$, indicating the $R^2CO_2^-$ anion binds strongly to the Mn_2 core. These results strongly suggest that the complexes **2-10** have similar structures to that of **1** with the $R^2CO_2^-$ bridging anion.

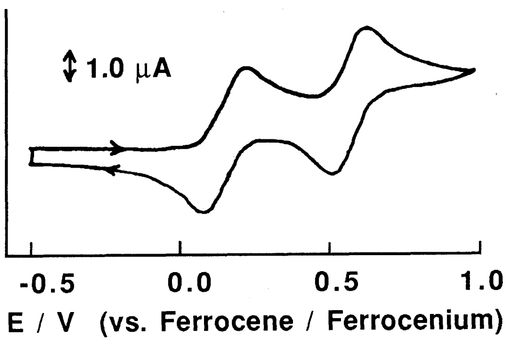


Fig. 3. Cyclic voltammogram of **1** in CH_3CN. 0.1 M $Et_4N{\cdot}ClO_4$. Scan rate 100 mV/s.

The cyclic voltammogram of **1** is shown in Fig. 3. It exhibited two quasi-reversible redox waves $E^1{}_{1/2}$ and $E^2{}_{1/2}$ at 0.15 V and 0.56 V (vs. Fc / Fc^+; Fc = Ferrocene) which were assigned to the redox couples of Mn_2(II, II) / Mn_2(II, III) and Mn_2(II, III) / Mn_2(III, III) respectively. The complexes **2-10** similarly showed two redox waves. When electron-withdrawing (donating) substituents were introduced at R^1 and /or R^2, both $E^1{}_{1/2}$ and $E^2{}_{1/2}$ showed anodic (cathodic) shifts. The $E^1{}_{1/2}$ values showed fairly good linear relationships with σ_p of R^1 (Fig. 4a) and pK_a's of R^2CO_2H (Fig. 4b).[8], suggesting these potential changes are mainly due to electronic effects rather than structural changes. In the case of **10** (R^1=Br, R^2=F_3C), $E^1{}_{1/2}$ shifted up to 0.35 V (vs. Fc / Fc^+) which is 200 mV higher than **1**, and this amount of anodic shift is roughly the sum of those for **5** (R^1=CH_3, R^2=F_3C) (120 mV) and **9** (R^1=Br, R^2=CH_3) (110 mV), indicating additivity of the electronic effects of the ligating anion and the substituent on the phenol ring. These results suggest that the redox properties of a series of dinuclear Mn(II) complexes $[R^1\text{-}LMn_2(R^2CO_2)]ClO_4$ can be controlled so finely by a combination of carboxylate anion and substituent at 4-position of the phenol ring. Such "fine-tuning" of redox properties may be useful to construct functional models of Mn-containing redox enzymes.

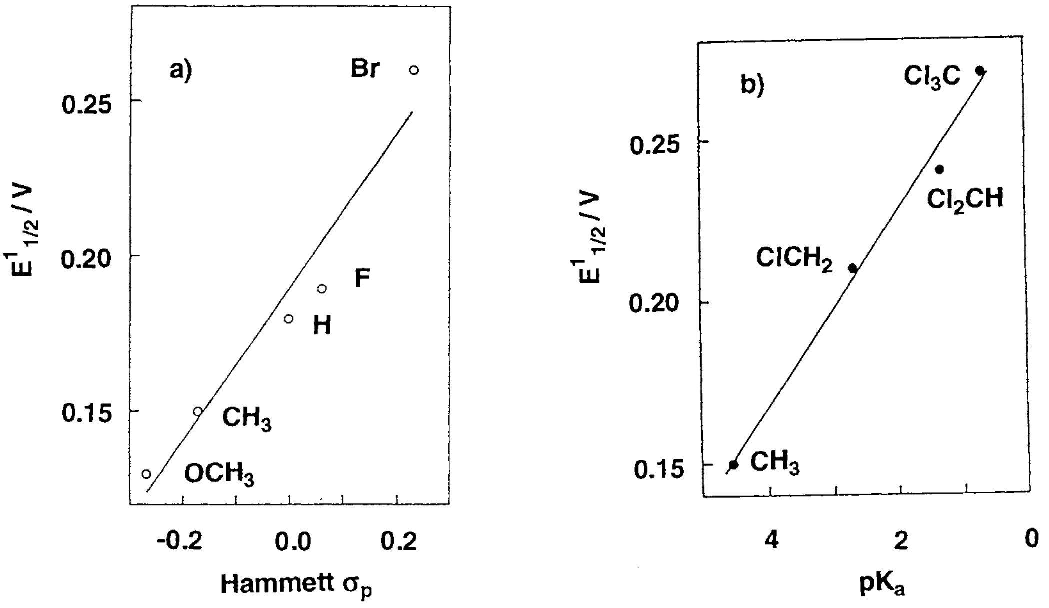


Fig. 4. a) Plot of $E^1{}_{1/2}$ of $[R^1\text{-}LMn_2(CH_3CO_2)]ClO_4$ vs. Hammett σ_p of R^1.
b) Plot of $E^1{}_{1/2}$ of $[CH_3\text{-}LMn_2(R^2CO_2)]ClO_4$ vs. pK_a of R^2CO_2H.

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References

1) L. Que. Jr. and A. E. True, *Prog. Inorg. Chem.*, **38**, 97 (1990).

2) V. V. Barynin and A. I. Grebenko, *Dokl. Akad. Nauk. SSR*, **288**, 1100 (1986), and references therein.

3) N. Murata, M. Miyao, T. Omata, H. Matsunami, and T. Kuwabara, *Biochim. Biophys. Acta*, **765**, 363 (1984); G. W. Brudvig, H. H. Thorp, and R. H. Crabtree, *Acc. Chem. Res.*, **24**, 311 (1991).

4) D. N. Hendrickson, G. Christou, E. A. Schmitt, E. Libby, J. S. Dashkin, S. Wang, H.-L. Tsai, J. B. Vincent, P. D. W. Boyed, J. C. Huffman, K. Folting, Q. Li, and W. E. Streib, *J. Am. Chem. Soc.*, **114**, 2455 (1992); P. A. Gooson, A. R. Oki, J. Glerup, and D. J. Hodgson, *ibid.*, **112**, 6248 (1990); S.-B. Yu, S. J. Lippard, I. Shweky, and A. Bino, *Inorg. Chem.*, **31**, 3502 (1992); D. M. Eichhorn and W. H. Armstrong, *J. Chem. Soc., Chem. Comm.*, **1992**, 85; E. Larson, M. S. Lah, X. Li, J. A. Bonadies, and V. L. Pecoraro, *Inorg. Chem.*, **31**, 373 (1992); C. Flessbeck, K. Wieghardt, E. Bill, C. Butzlaff, A. X. Trantwein, B. Nuber, and J. Weiss, *ibid.*, **31**, 21 (1992); N. Aurangzeb, C. E. Hulme, C. A. McAuliffe, R. G. Pritchard, M. Watkinson, A. Garcia-Deibe, M. R. Bermejo, and A. Sousa, *J. Chem. Soc., Chem. Comm.*, **1992**, 1524; G. C. Dailey, C. P. Horwitz, and C. A. Lisek, *Inorg. Chem.*, **31**, 5325 (1992); M. Osawa, U. P. Singh, M. Tanaka, Y. Moro-oka, and N. Kitajima, *J. Chem. Soc., Chem. Comm.*, **1993**, 310; M. Mikuriya, Y. Yamato, and T. Tokii, *Chem. Lett.*, **1991**, 1429; M. Mikuriya, Y. Yamamoto, and T. Tokii, *Inorg. Chim. Acta*, **181**, 1 (1991); N. Matsumoto, J. J. Zhong, H. Okawa, and S. Kida, *ibid.*, **160**, 153 (1989); K. Shindo, Y. Mori, K. Motoda, H. Sakiyama, N. Matsumoto, and H. Okawa, *Inorg. Chem.*, **31**, 5325 (1992); M. Suzuki, T. Sugisawa, H.Senda, H. Oshio, and A. Uehara, *Chem. Lett.*, **1989**, 1091; M. Suzuki, Y. Hayashi, K. Munezawa, M. Suenaga, H. Senda, and A. Uehara, *ibid.*, **1991**, 1429; Y. Nishida and M. Nasu, *Inorg. Chim. Acta*, **190**, 1 (1991). For reviews see: K. Wieghardt, *Angew. Chem., Int. Ed. Engl.*, **28**, 1153, (1989); G. Christou, *Acc. Chem. Res.*, **22**, 328 (1989).

5) N. H. Pilkington and R. Robson, *Aust. J. Chem.*, **23**, 225 (1970).

6) Crystal Data of $[CH_3\text{-}LMn_2(CH_3CO_2)]ClO_4 \cdot DMF$: $C_{32}H_{46}N_7O_9ClMn_2$, F.W.= 830.11, Monoclinic, *P2/m*, a = 17.088(4), b = 10.964(4), c = 20.747(3) Å, β = 92.56(2)°, V =3883(2) Å^3, Z = 4, D_c = 1.419 g cm^{-3}, μ(Mo Kα) = 7.49 cm^{-1}, R = 8.29 %, R_w = 10.2 %. Total of 5102 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the analysis.

7) Dinuclear Mn(II) complexes with potentially octadentate (N_4O_4) Robson-type ligands were reported. D. Luneau, J.-M. Savariault, P. Cassoux, and J.-P. Tuchagues, *J. Chem. Soc., Dalton Trans.*, **1988**, 1225; A. J. Downard, V. Mckee, and S.S. Tandon, *Inorg. Chim. Acta*, **173**, 181 (1990). In these complexes, however, the macrocyclic ligands were actually hexadentate (N_4O_2), and each Mn ion had two sites for external anions to bind. Our complex is unique in the point that the macrocyclic ligand is actually octadentate and leaves only one binding site per Mn ion for external ligands.

8) Similar relationships have been observed in the case of mononuclear Mn(IV) complexes. H. Okawa, M. Nakamura, and S. Kida, *Bull. Chem. Soc. Jpn.*, **55**, 466 (1982); M. Koikawa and H. Okawa, *J. Chem. Soc., Dalton Trans.*, **1988**, 641.

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