A Binuclear Manganese(II) Complex with 2,6-Bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol

MASAHIRO MIKURIYA*, YASUSHI KAWASAKI

Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662, Japan

TADASHI TOKII

Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan

SATOSHI YANAI and ASAKO KAWAMORI

Department of Physics, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662, Japan

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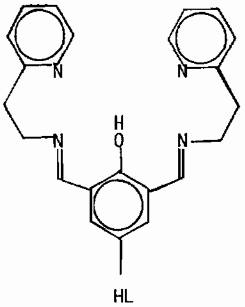
Binuclear manganese complexes have attracted considerable attention because of their possibility as models for the oxygen-evolving center of the photosystem II [1]. However, only a few binuclear manganese complexes have been reported, although some examples have appeared very recently [2–15]. One of the difficulties in the synthesis of binuclear manganese complexes is caused by misunderstanding of their analytical data, since the manganese complexes often show complicated compositions. In this study we have isolated one of such complexes by using a binucleating ligand, 2,6-bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol (HL). The elemental analyses suggested that the complex has the composition $Mn_2(L)(CH_3O)(CH_3COO)(ClO_4)(CH_3OH)$. The binuclear structure has been characterized on the basis of IR, electronic and ESR spectra, and magnetic susceptibilities (80–300 K).



HL

The complex was prepared as follows. 2,6-Diformyl-4-methylphenol (prepared according to the method of Okawa and Kida [16]) (80 mg) and 2-(2-aminoethyl)pyridine (122 mg) were dissolved in 10 ml of methanol. Then manganese(II) acetate tetrahydrate (245 mg) and $NaClO_4$ (367 mg) were successively added. The mixture was stirred and filtered; a slow evaporation gave yellow crystals. *Anal.* Found: C, 45.86; H, 4.62; N, 7.58; Mn, 15.58. Calc. for $Mn_2(C_{23}H_{23}N_4O)(CH_3O)(CH_3COO)(ClO_4)(CH_3OH)$: C, 46.14; H, 4.73; N, 7.97; Mn, 15.63%.

The presence of ClO_4^-, CH_3COO^- and CH_3OH is suggested from the IR spectrum of the complex. The ν(Cl–O) bands of ClO_4^- appear at 1050–1150 cm^{-1}. The small splittings of these bands indicate that the coordination of ClO_4^- to metal ion is not strong, even if the manganese ion is coordinated by the perchlorate ion. The $\nu_a(COO^-)$ and $\nu_s(COO^-)$ bands of CH_3COO^- appear at 1588 and 1441 cm^{-1}, respectively. The $\Delta\nu$ value between them falls in the range of those observed for a symmetrically bridging carboxylate group [2, 8, 10]. A broad band around 3440 cm^{-1} may be attributable to the ν(O–H) band of semi-coordinated or crystal methanol. Based on the elemental analyses and the IR spectral data, we can assume the complex has the binuclear structure shown in Fig. 1. This structure is not unprecedented. Recently we [10] and Nishida *et al.* [11] have independently found a similar structure in the X-ray crystal structures of $[Mn_2(L')(CH_3O)(CH_3COO)(ClO_4)(CH_3OH)]$ (L′ = 1,5-bis(salicylideneamino)-3-pentanol and 1,5-bis(5-chlorosalicylideneamino)-3-pentanol).

The electronic spectrum of the complex in acetonitrile shows no appreciable absorption in the region below 20 × 10^3 cm^{-1}, indicating the electronic configuration of the manganese(II) ion is of high-spin. In the high-frequency region, two strong bands arising from the Schiff base ligand are observed at 26.5 × 10^3 cm^{-1} (ϵ = 7950 mol^{-1} dm^3 cm^{-1}) and 38.9 × 10^3 cm^{-1} (ϵ = 36 930 mol^{-1} dm^3 cm^{-1}).

In order to confirm the binuclear structure, the magnetic susceptibilities were measured over the temperature range 80–300 K and the result is shown in Fig. 2. The magnetic moment of the complex is 5.46 B.M./Mn at room temperature, which is lower than those of normal high-spin manganese(II) complexes. The magnetic data were analyzed with the

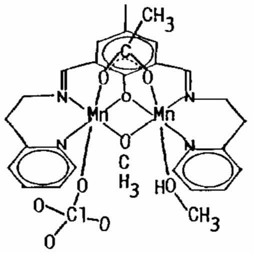


Fig. 1. Proposed structure of $Mn_2(L)(CH_3O)(CH_3COO)(ClO_4)(CH_3OH)$.

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*Author to whom correspondence should be addressed.

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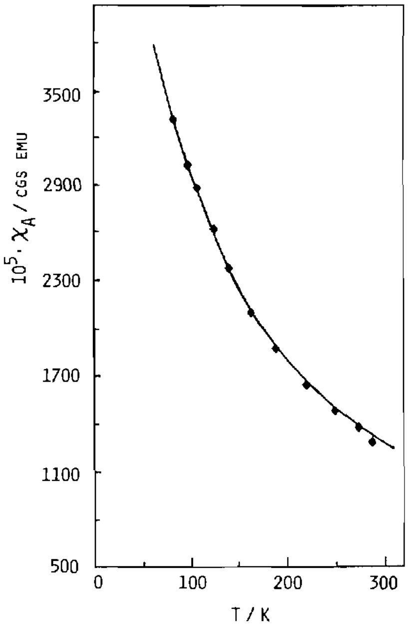

Fig. 2. Temperature dependence of the magnetic susceptibilities of $Mn_2(L)(CH_3O)(CH_3COO)(ClO_4)(CH_3OH)$.

Van-Vleck equation for the $(S = 5/2)$–$(S = 5/2)$ system based on the Heisenberg model:

$$\chi_A = \frac{Ng^2\beta^2}{kT} \times \frac{55 + 30X^{10} + 14X^{18} + 5X^{24} + X^{28}}{11 + 9X^{10} + 7X^{18} + 5X^{24} + 3X^{28} + X^{30}}$$

where $X = \exp(-J/kT)$ and the other symbols have their usual meanings. The solid curve in Fig. 2 is the curve calculated by using the parameters $J = -3.8$ cm^{-1} and $g = 1.99$. This indicates that the two high-spin manganese(II) ions are antiferromagnetically coupled. The antiferromagnetic spin–exchange interaction in the complex is comparable to that of $[Mn_2(L')(CH_3O)(CH_3COO)(ClO_4)(CH_3OH)]$ ($J = -10.6$ cm^{-1}) [11].

The X-band ESR spectra of the complex in acetonitrile (at 102 and 295 K) showed two broad resonances centered near $g = 4.3$ and 2.0.

References

1 K. Sauer, *Acc. Chem. Res., 13*, 249 (1980).
2 N. Torihara, M. Mikuriya, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn., 53* (1980) 1610; M. Mikuriya, N. Torihara, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn., 54* (1981) 1063.
3 K. Wieghardt, U. Bossek, D. Ventur and J. Weiss, *J. Chem. Soc., Chem. Commun.*, (1985) 347; K. Wieghardt, U. Bossek, J. Bonvoisin, P. Beauvillan, J.-J. Girerd, B. Nuber, J. Weiss and J. Heinze, *Angew. Chem., Int. Edn. Engl., 25* (1986) 1030; K. Weighardt, U. Bossek, L. Zsolnai, G. Huttner, G. Blondin, J.-J. Girerd and F. Babonneau, *J. Chem. Soc., Chem. Commun.*, (1987) 651.
4 J. B. Vincent, K. Folting, J. C. Huffman and G. Christou, *Inorg. Chem., 25* (1986) 996; J. S. Bashkin, A. R. Schake, J. B. Vincent, H.-R. Chang, Q. Li, J. C. Huffman, G. Christou and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, (1988) 700.
5 J. E. Sheats, R. S. Czernuszewicz, G. C. Dismukes, A. L. Rheingold, V. Petrouleas, J. Stuble, W. H. Armstrong, R. H. Beer and S. J. Lippard, *J. Am. Chem. Soc., 109* (1987) 1435.
6 P. Mathur, M. Crowder and G. C. Dismukes, *J. Am. Chem. Soc., 109* (1987) 5227.
7 D. P. Kessissoglou, W. M. Butler and V. L. Pecoraro, *Inorg. Chem., 26* (1987) 495.
8 M. Suzuki, S. Murata, A. Uehara and S. Kida, *Chem. Lett.*, (1987) 281; M. Suzuki, M. Mikuriya, S. Murata, A. Uehara, H. Oshio, S. Kida and K. Saito, *Bull. Chem. Soc. Jpn., 60* (1987) 4305.
9 Y. Nishida, *Chem. Lett.*, (1987) 2151.
10 M. Mikuriya, S. Kida and I. Murase, *Chem. Lett.*, (1988) 35.
11 Y. Nishida, N. Oshino and T. Tokii, *Z. Naturforsch., Teil B, 43* (1988) 472.
12 R. M. Buchaman, K. J. Oberhausen and J. F. Richardson, *Inorg. Chem., 27* (1988) 971.
13 H. Diril, H.-R. Chang, X. Zhang, S. K. Larsen, J. A. Potenza, C. G. Pierpont, H. J. Schugar, S. S. Isied and D. N. Hendrickson, *J. Am. Chem. Soc., 109* (1987) 6207; H.-R. Chang, H. Diril, M. J. Nilges, X. Zhang, J. A. Potenza, H. J. Schugar, D. N. Hendrickson and S. S. Isied, *J. Am. Chem. Soc., 110* (1988) 625; H.-R. Chang, S. K. Larsen, P. D. W. Boyd, C. G. Pierpont and D. N. Hendrickson, *J. Am. Chem. Soc., 110* (1988) 4565.
14 M. A. Collins, D. J. Hodgson, K. Michelsen and D. K. Towle, *J. Chem. Soc., Chem. Commun.*, (1987) 1659; K. S. Hagen, W. H. Armstrong and H. Hope, *Inorg. Chem., 27* (1988) 967; D. K. Towle, C. A. Botsford and D. J. Hodgson, *Inorg. Chim. Acta, 141*, (1988) 167; M. Suzuki, S. Tokura, M. Suhara and A. Uehara, *Chem. Lett.*, (1988) 477.
15 D. Luneau, J.-M. Savariault, P. Cassoux and J.-P. Tuchagues, *J. Chem. Soc., Dalton Trans.*, (1988) 1225.
16 H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn., 45* (1972) 1759.