CHEMISTRY LETTERS, pp. 1181-1184, 1990.

Synthesis, Structures, and Magnetic Properties of Novel Binuclear and Mononuclear Manganese(II) Complexes with 2,6-Bis[N-(2-pyridylethyl)iminomethyl]-4-methylphenol

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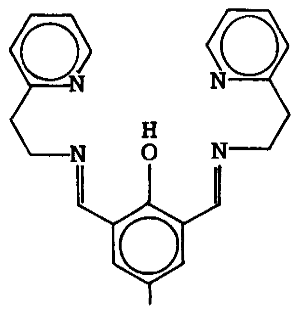
Binuclear and mononuclear manganese(II) complexes with 2,6-bis[N-(2-pyridylethyl)iminomethyl]-4-methylphenol (HL), $[Mn_2(L)(CH_3COO)_2(NCS)]$ and $[Mn(HL)(NCS)_2(H_2O)]$, have been prepared and characterized by X-ray structure analyses, magnetic susceptibilities (80—300 K), and EPR spectrum.

Binuclear manganese complexes are of current interest because such systems are known to exist at the active site of some manganese-containing enzymes such as the photosystem II of green plants and the catalase from *Lactobacillus plantarum*.1) Recently we have prepared a binuclear manganese(II) complex using a binucleating ligand, 2,6-bis[N-(2-pyridylethyl)-iminomethyl]-4-methylphenol (HL). This complex has a complicated composition and the two manganese(II) ions are antiferromagnetically coupled.2) During the course of our studies on manganese complexes with this ligand, we have found that reaction with thiocyanate ion leads to formation of a novel binuclear manganese(II) complex with different coordination environments, $[Mn_2(L)(CH_3COO)_2(NCS)]$ (**1**), and a unique mononuclear manganese(II) complex, $[Mn(HL)(NCS)_2(H_2O)]$ (**2**). Here we report the syntheses, X-ray crystal structures, and magnetic properties of these complexes.


HL

The binuclear manganese(II) complex **1** was prepared as follows. 2,6-Diformyl-4-methylphenol

(0.2 mmol) and 2-(2-aminoethyl)pyridine (0.4 mmol) were dissolved in 4 ml of methanol. Then manganese(II) acetate tetrahydrate (0.4 mmol) and ammonium thiocyanate (0.4 mmol) were successively added. The reaction mixture was refluxed with stirring for 30 min. The solution was filtered while hot; a slow evaporation gave orange crystals (67% yield).3)

The structure of **1** was determined by X-ray crystallography.4) The crystal contains two crystallographically independent binuclear molecules; they are represented as A and B. Their structures are essentially the same. A perspective view of A is illustrated in Fig. 1. The striking feature of this structure is that the two manganese environments are different. The two manganese ions are bridged by a phenoxide oxygen of the binucleating ligand L and two acetate ions (Mn1---Mn2 av. 3.341(2) Å). The coordination geometry of Mn1 is a distorted square pyramid. The basal plane is formed by N1, N2, O1, and O4 atoms from the ligand L and one acetate ion, and the fifth coordination site is occupied by O2 atom of the other acetate ion. On the other hand, the manganese ion Mn2 is in an N_3O_3 octahedral environment formed by the ligand L, two acetate ions, and a thiocyanate ion. The Mn-O (2.069(6)–2.197(5) Å) and Mn-N (2.195(6)–2.294(6) Å) lengths fall within the range typically found for manganese(II) complexes.5) Considering the trend of manganese ion toward six-coordination, this is a novel example of binuclear complexes having different coordination environments with a symmetric binucleating ligand.

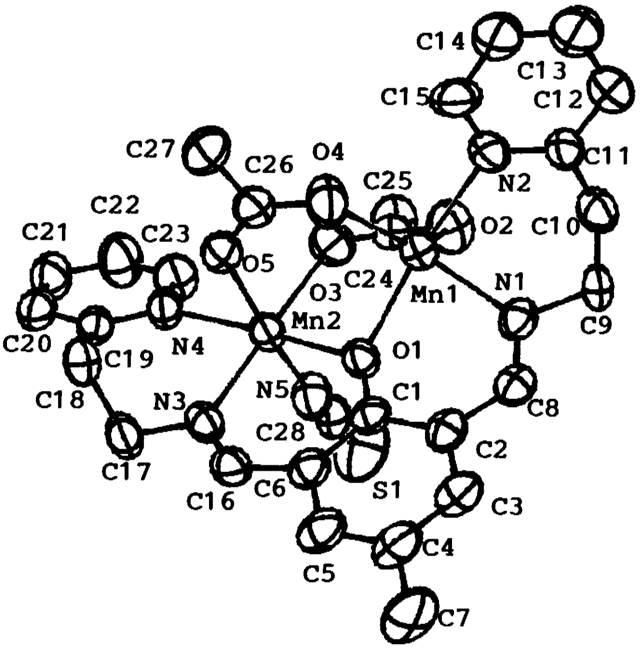


Fig. 1. Perspective view of $[Mn_2(L)(CH_3COO)_2(NCS)]$ (molecule A). Selected bond lengths (l/Å) and angles (φ/°): Mn1---Mn2 3.337(2), 3.344(2); Mn1-O1 2.178(5), 2.149(5); Mn1-O2 2.158(6), 2.112(6); Mn1-O4 2.069(6), 2.069(6); Mn1-N1 2.198(6), 2.207(6); Mn1-N2 2.294(6), 2.289(6); Mn2-O1 2.181(5), 2.197(5); Mn2-O3 2.145(6), 2.132(7); Mn2-O5 2.196(5), 2.183(5); Mn2-N3 2.207(6), 2.202(6); Mn2-N4 2.278(7), 2.282(7); Mn2-N5 2.195(6), 2.205(7); Mn1-O1-Mn2 99.9(2), 100.6(2) for molecules A and B, respectively.

The magnetic moment of **1** is 5.60 B.M./Mn at 297 K, which is lower than the spin-only value for high-spin d^5 electronic configuration. The magnetic susceptibility data (80–300 K) were analyzed with the Van-Vleck equation based on the

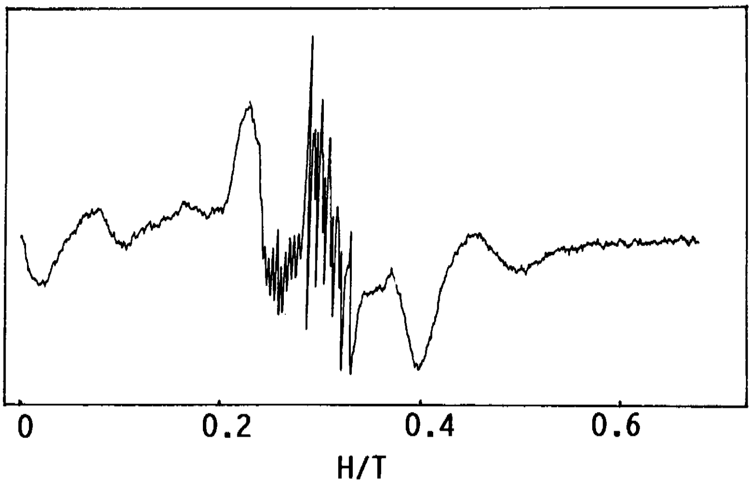


Fig. 2. X-Band EPR spectrum of $[Mn_2(L)(CH_3COO)_2(NCS)]$, DMF/toluene glass at 10 K.

Heisenberg model ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ ($S_1 = S_2 = 5/2$)) and the best fitting parameters are $J = -2.5$ cm^{-1} and $g = 2.00$. This indicates that an antiferromagnetic interaction is operating between the two manganese(II) ions. The frozen solution EPR spectrum of **1** shows a multiline in the range 230—350 mT (Fig. 2). This is a rare example of binuclear manganese(II) complexes which show a multiline EPR signal. Such multiline feature may arise from the magnetic interaction between the two manganese(II) ions.[6)]

It is interesting that only one thiocyanate ion is trapped in a binuclear unit under the reaction of the binucleating ligand HL, manganese(II) acetate, and ammonium thiocyanate with the 1:2:2 molar ratio. In order to attain the formation of a six-coordinate binuclear complex where both manganese(II) ions are coordinated by thiocyanate ions, we used an excess of thiocyanate ion under the same preparative condition as that for **1** except for the amount of NH_4SCN. However, a mononuclear manganese(II) complex **2** was obtained as vermilion crystals from the reaction mixture of 2,6-diformyl-4-methylphenol (0.2 mmol), 2-(2-aminoethyl)pyridine (0.4 mmol), manganese(II) acetate tetrahydrate (0.4 mmol), and ammonium thiocyanate (2.0 mmol) in methanol (76% yield).[3,7)] The magnetic moment of **2** (5.92 B.M./Mn at 287 K) is close to those for normal high-spin manganese(II) complexes and the magnetic susceptibility data (80—300 K) obey the Curie law. The X-ray structure determination of **2** revealed a

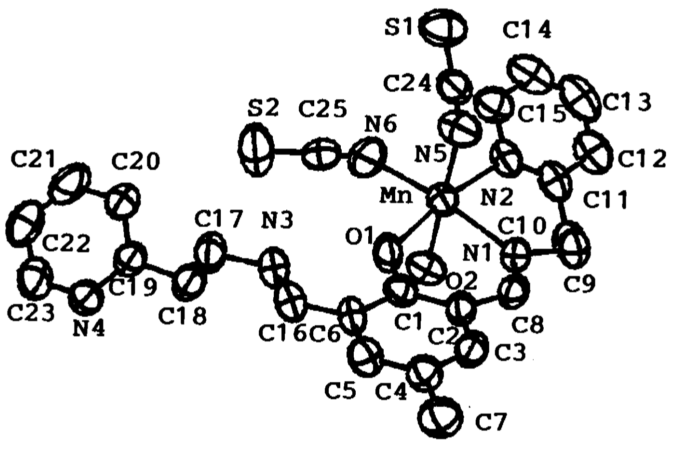


Fig. 3. Perspective view of $[Mn(HL)(NCS)_2(H_2O)]$. Selected bond lengths (l/Å): Mn-O1 2.141(4), Mn-O2 2.268(4), Mn-N1 2.230(5), Mn-N2 2.270(5), Mn-N5 2.214(6), Mn-N6 2.148(7).

unique mononuclear structure where the octahedral coordination around the manganese ion is formed by six donor atoms (N_4O_2) of the binucleating ligand HL, two thiocyanate ions, and a water molecule.[4] One of the side-arm pyridine nitrogens of the binucleating ligand is not coordinated.[8]

The present results show a flexible complexation of the binucleating ligand, 2,6-bis[N-(2-pyridylethyl)iminomethyl]-4-methylphenol.

References

1) K. Sauer, *Acc. Chem. Res.*, **13**, 249 (1980); R. M. Fronko, J. E. P.-Hahn, and C. J. Bender, *J. Am. Chem. Soc.*, **110**, 7554 (1988).

2) M. Mikuriya, Y. Kawasaki, T. Tokii, S. Yanai, and A. Kawamori, *Inorg. Chim. Acta*, **156**, 21 (1989).

3) A satisfactory analysis (C, H, N) has been obtained.

4) Crystal data for **1**: $C_{28}H_{29}Mn_2N_5O_5S$, F.W. = 657.5, monoclinic, space group $P2_1/c$, $a = 21.220(11)$, $b = 15.947(2)$, $c = 17.912(10)$ A, $\beta = 101.38(3)°$, $V = 5942.1(46)$ A^3, $Z = 8$, $D_m = 1.45$, $D_c = 1.47$ g cm^{-3}, μ(Mo-Kα) = 9.27 cm^{-1}, $R = 0.057$, $R_w = 0.064$. 10208 Reflections were measured in the range $2 \leq 2\theta \leq 48°$; 5948 with $I \geq 3\sigma(I)$ were assumed observed. For **2**: $C_{25}H_{26}MnN_6O_2S_2$, F.W. = 561.6, monoclinic, space group $P2_1/n$, $a = 9.289(3)$, $b = 19.685(5)$, $c = 14.670(5)$ A, $\beta = 94.86(2)°$, $V = 2672.9(15)$ A^3, $Z = 4$, $D_m = 1.38$, $D_c = 1.40$ g cm^{-3}, μ(Mo-Kα) = 6.49 cm^{-1}, $R = 0.054$, $R_w = 0.059$. 3499 Reflections were measured in the range $1 \leq 2\theta \leq 48°$; 2461 with $I \geq 3\sigma(I)$ were assumed observed. For the determination of both structures, intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. The structures were solved by direct methods and refined by the full-matrix least-squares methods using the SDP program package. H-atoms were not included in the calculations for **1** but done for **2**.

5) B. Mabad, P. Cassoux, J.-P. Tuchagues, and D. N. Hendrickson, *Inorg. Chem.*, **25**, 1420 (1986).

6) Molar conductance datum indicates that the complex **1** is 1:1 electrolyte in DMF. Therefore, the thiocyanate ion may be replaced by the solvent molecule in the EPR frozen solution.

7) The complex **2** was also obtained from the reaction of the complex **1** with ammonium thiocyanate (9 equiv.) in methanol.

8) M. Mikuriya, K. Kushida, H. Nakayama, W. Mori, and M. Kishita, *Inorg. Chim. Acta*, **165**, 35 (1989).

(Received April 23, 1990)