# A Novel Ferromagnetically Coupled Dinuclear Manganese(II) Complex with Phenoxo Bridges

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The reaction of $MnCl_2{\cdot}4H_2O$ with a tetradentate ligand yielded a dinuclear manganese(II) complex of $[Mn^{II}_2(H_2L)_2Cl_2]$ (**1**) ($H_3L$ = *N*-(2-hydroxy-5-nitrobenzyl)iminodiethanol). The magnetic susceptibility measurement revealed that **1** has an $S = 5$ spin ground state due to an intramolecular ferromagnetic interaction.

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In recent years manganese cluster chemistry is of great interest from view points of bioinorganic and physical chemistry. Dinuclear manganese complexes were used as models of a Mn catalase,[1] and tetranuclear complexes were known to exist at the active center for photosynthetic water oxidation.[2] In a field of magnetic materials, polynuclear manganese complexes with large spin multiplicity and uniaxial magnetic anisotropy have attracted an attention for solid-sate properties such as superparamagnetism and quantum spin tunneling.[3] A family of dodecanuclear Mn(III, IV) clusters have been proven to be single molecule magnets.[4] From the viewpoints of constructing such compounds, ferromagnetically coupled dinuclear manganese compounds are considered to be not only the simplest models for understanding magnetic interactions between metal centers, but also paramagnetic building units of polymeric architectures.[5] Numerous dimeric manganese(II) complexes have been synthesized,[6] but ferromagnetically coupled ones are relatively rare.[7] Herein, we report synthesis, structure, and magnetic property of a ferromagnetically coupled dinuclear manganese complex with tetradentate ligand.

The ligands $H_3L$ were obtained by following literature procedures.[8] $MnCl_2{\cdot}4H_2O$ (0.25 mmol) in MeOH (5 mL) was slowly added to the mixture of $H_3L$ (0.25 mmol) and $NEt_3$ (0.25 mmol) in MeOH (10 mL). Yellow crystals of $[Mn^{II}_2(H_2L)_2Cl_2]$ (**1**)[9] were obtained by slow diffusion of acetone into the reaction mixture.

Structure of **1** is displayed in Figure 1. **1** crystallized in triclinic space group $P\bar{1}$ composed of a dinuclear unit and has an inversion center. Coordination geometry about each manganese(II) ion is a significantly distorted octahehedron with $N_1O_4Cl_1$ chromospheres provided by a chloride ion and tetradentate monoanionic ligands ($H_2L^-$), in which alkylalcohol groups are protonated. The valence of each manganese ion is 2+, which is confirmed by the coordination bond lengths (2.163(2)–2.476(1) Å) and the valence sum calculations. The bond lengths between manganese ion and phenoxy groups (Mn–O1 = 2.167(2), Mn–O1* = 2.163(2) Å) are slightly shorter than those between manganese ion and alkylalcohol oxygen atoms (Mn–O2 = 2.223(3), Mn–O3 = 2.214(3) Å). The remaining coordination bond lengths are 2.337(3) Å for the Mn–N bond and 2.476(1) Å for the Mn–Cl bond, respectively. The two manganese(II) ions are doubly bridged by the phenoxo groups with the Mn···Mn separation of 3.443(2) Å.

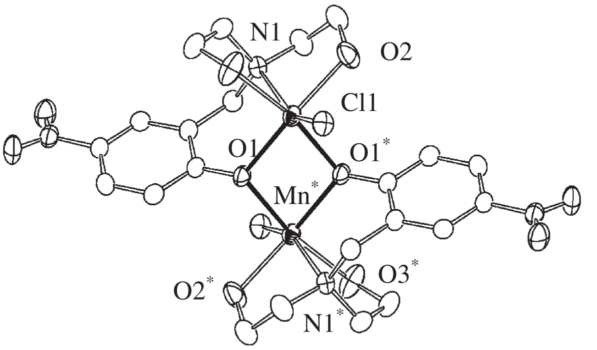

**Figure 1.** ORTEP diagram of **1**. Selected interatomic distances (Å) for **1**: Mn–O1 2.167(2), Mn–O1* 2.163(2), Mn–O2 2.223(3), Mn–O3 2.214(2), Mn–N 2.337(3), Mn–Cl 2.476(1). Key to symmetry operation of *: $-x+1$, $-y+1$, $-z+2$.

Temperature dependence of magnetic susceptibility with applying magnetic field of 0.1 T was measured down to 1.8 K for **1**, and the results are depicted in the form of a $\chi_m T$ vs temperature plot (Figure 2). The $\chi_m T$ value at 300 K is 8.73 emu mol$^{-1}$ K, which is close to the value expected for uncorrelated two manganese(II) ions (8.75 emu mol$^{-1}$ K for $g = 2$). Upon cooling, the $\chi_m T$ values gradually increased to a maximum value of 9.64 emu mol$^{-1}$ K at 15 K, which is indicative of ferromagnetic interactions occurring between two manganese(II) ions. A sudden decrease of $\chi_m T$ values below 14 K is due to intermolecular antiferromagnetic interactions. Magnetization data for **1** were collected as a function of applied magnetic field up to 5 T at 1.9 K. The $M/N\mu_B$ values increased with increasing magnetic field and reached a value of 9.53 at 5 T, which suggests an $S = 5$ spin ground state for **1**. The magnetic susceptibility data were analyzed by a two spin model with a coupling constant $J$ ($H = -2JS_1 \cdot S_2$).[10] The least squares calculation by using the data above 26 K gave the best fit parameters of $g = 1.988(4)$, $J = +0.31(3)$ cm$^{-1}$. Although the ferromagnetic interactions were observed in some alkoxo and phenoxo-bridged manganese complexes, $Mn_2LX_2$ (L = Robson-type macrocyclic ligands, X = $N_3^-$, $Cl^-$, or $Br^-$),[7] the antiferromagnetic intractions were generally propagated via phenoxo bridges.[6] Magnetic interactions between manganese ions occur by superexchanges through phenoxo-oxygen atoms, which give ferromagnetic and antiferromagnetic contributions. It is difficult to predict the magnetic interactions by using structural parameters, however, Mn–O1–Mn bond with the angle of 105.35(7)° diminish overlaps between oxygen p$\sigma$ and manganese d$\sigma$ orbitals and might be responsible for the occurrence of the ferromagnetic interactions in **1**.

In summary, we prepared ferromagnetically coupled dinuclear manganese(II) complex **1**, and structure and magnetic

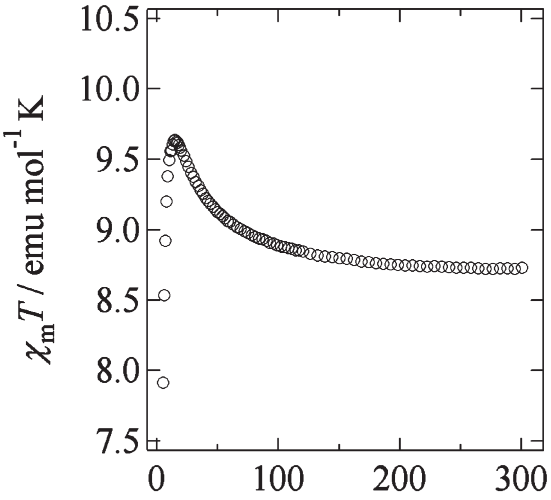

**Figure 2.** $\chi_m T$–$T$ plot for **1**.

property were studied. In **1** further deprotonation of the ligand may give an opportunity to build larger alkoxo-bridged manganese clusters.

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We dedicate this article to Professor Philipp Gütlich for his 70th birthday.

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9 Crystal data: **1**: $C_{22}H_{30}Cl_2Mn_2N_4O_{10}$, $M_r = 691.28$, triclinic space group $P\bar{1}$, $a = 8.197(3)$, $b = 8.500(3)$, $c = 10.940(4)$ Å, $\alpha = 78.103(7)$, $\beta = 88.613(8)$, $\gamma = 65.000(7)°$, $V = 674.3(4)$ Å$^3$, $Z = 1$, $T = -70$ °C. A total of 3151 were collected ($3° < 2\theta < 50°$) of which 1930 unique refrections ($R_{int} = 0.0185$) were measured. Residual $R$ and $wR$ were 0.0378 and 0.0885, respectively, from the refinement on $F^2$ with $I > 2\sigma(I)$. In the structure analyses, non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Anal. Calcd for $C_{22}H_{30}Cl_2Mn_2N_4O_{10}$: C, 38.22; H, 4.37; N, 8.10%. Found: C, 38.41; H, 4.59; N, 8.06%.

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