Syntheses and Magnetic Properties of Cyclic Tetranuclear and Infinite Linear-chain Copper(II)–Manganese(II) Complexes

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Two heterometal assemblies, [$Cu^{II}L^2Mn^{II}$(hfac)] (**2**) and [$Cu^{II}L^3Mn^{II}$(hfac)] (**3**), have been synthesized by the assembly reaction of "bridging ligand-complex" Na[$Cu^{II}L^n$] ($n = 2$, 3) and [$Mn^{II}(hfac)_2(H_2O)_2$], where H_3L^2 = 1-(2-hydroxy-3-methoxybenzamido)-2-(2-hydroxybenzylideneamino)ethane, H_3L^3 = 1-(2-hydroxy-3-methoxybenzamido)-2-(2-hydroxy-3-methoxybenzylideneamino)ethane, and Hhfac = hexafluoroacetylacetone. The temperature-dependent magnetic susceptibility and field-dependent magnetization data demonstrated that **3** was well-reproduced by a cyclic tetranuclear structure, while those of **2** indicated an infinite linear chain structure.

Magnetochemistry on heterometal polynuclear complexes has attracted much attention for a long time both from the material science and model study of metal enzymes.[1] A number of discrete heterometal polynuclear complexes have been synthesized and their magnetic properties have been extensively investigated.[2] In the latest two decades, a number of versatile molecular-based magnetic materials exhibiting three-dimensional magnetic ordering have been synthesized from the assembly reaction of the two building components.[3] Recently we have reported a series of heterometal cyclic tetranuclear compounds, [$Cu^{II}L^1M^{II}$(hfac)]$_2$ (**1**), where [$Cu^{II}L^1$]$^-$ (H_3L^1 = 1-(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxybenzylideneamino)ethane) is a donor building component that functions "bridging ligand-complex" and [$M^{II}(hfac)_2(H_2O)_2$] is an acceptor building component exhibiting substitutable coordination sites.[3] The phenoxo and methoxy oxygen atoms of the Cu^{II} component coordinate to one M^{II} ion, and the amide oxygen atom at the opposite side further coordinates to another M^{II} ion. As the result, a cyclic tetranuclear structure is constructed. Various assembly structures may be achieved by selecting the ligand-complex, because the steric repulsion between the adjacent Cu^{II} and M^{II} species would be an important factor to determine the final assembly structure. From this viewpoint, the ligand of the Cu^{II} complex was modified in the hope that the variety of the assembly structures can be generated. For this purpose, three ligand-complexes with unequivalent tetradentate ligands H_3L^n ($n = 1$, 2, 3) are examined. The ligand H_3L^2 is an isomer of H_3L^1, in which a methoxy group is substituted at 3-position of 2-hydroxybenzamido moiety for H_3L^2, while a methoxy group is substituted at 3-position of salicylaldehyde moiety for H_3L^1. For the ligand H_3L^3, two methoxy groups are attached at the two positions. We report here the syntheses and magnetic properties of a cyclic tetranuclear and a linear-chain Cu^{II}–Mn^{II} assemblies, [$Cu^{II}L^2Mn^{II}$(hfac)] (**2**) and [$Cu^{II}L^3Mn^{II}$(hfac)] (**3**). Figure 1 shows the synthetic procedure and the proposed structures for **2** and **3**.

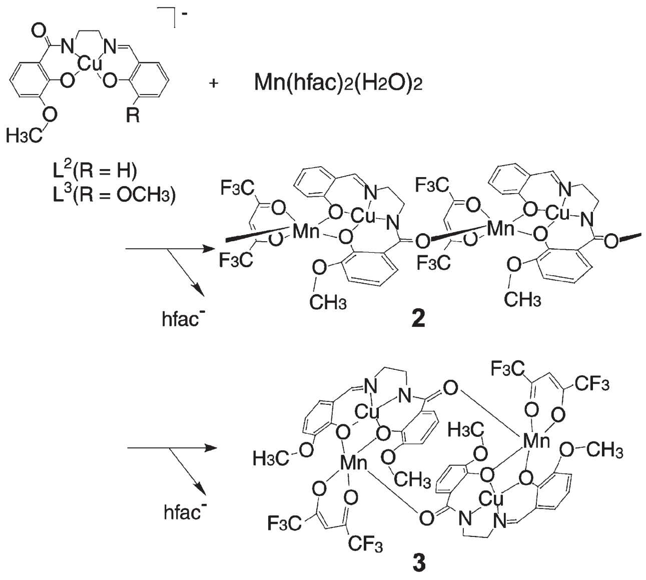

Figure 1. Synthetic scheme from the complementary component building blocks to the assembly structures.

The Cu^{II}–Mn^{II} heterometal complexes, **2** and **3** were synthesized by an assembly reaction of Na[$Cu^{II}L^n$] ($n = 2$, 3) and [$Mn^{II}(hfac)_2(H_2O)_2$]. The simple mixing of methanolic solutions of Na[$Cu^{II}L^n$] and [$Mn^{II}(hfac)_2(H_2O)_2$] with a 1:1 mole ratio gave heterometal complexes with the chemical formula [$Cu^{II}L^nMn^{II}$(hfac)] ($n = 2$, 3), where one hfac$^-$ ligand per Mn^{II} ion is eliminated during the reaction to give an electrically neutral species. Compounds **2** and **3** were obtained as fine needle-like and plate crystals, respectively.[4] Each infrared spectrum exhibits an intense absorption band around 1650 cm^{-1} assignable to the $\nu_{C=O}$ vibration of the amido moiety.

The magnetic susceptibilities were measured under a 1 T applied magnetic field in the 4–300 K temperature range.[5] The magnetic behavior is shown in Figure 2, as the $\chi_M T$ per Cu–Mn vs T plots. The $\chi_M T$ values for **2** and **3** at 300 K are 4.48 and 4.15 cm^3 K mol^{-1}, respectively, whose values are smaller than the spin-only value of 4.74 cm^3 K mol^{-1} expected for independently existing a Cu^{II} ($S = 1/2$) and a high-spin Mn^{II} ($S = 5/2$) ions and $g = 2.00$. On lowering the temperature, the $\chi_M T$ decreases gradually to reach a minimum, then increases to reach a maximum, and finally slightly decreases. The decrease at the higher temperature region indicates the operation of antiferromagnetic interaction between the Cu^{II} and Mn^{II} ions. The overall magnetic behaviors of **2** and **3** are similar to the previously reported cyclic tetranuclear Cu^{II}–Mn^{II} complex [CuL^{1}Mn^{II}(hfac)]$_2$.[3c] However, the maximum value of the $\chi_M T$ of **2**, 5.92 cm^3 K mol^{-1}, is larger than the spin-only value, 4.99 cm^3 K mol^{-1}/Cu–Mn expected for isolated $S = 4$ resulting from antiferromagnetic coupling between the Cu^{II} and Mn^{II} ions of a cyclic tetranuclear complex, while the maximum value of the $\chi_M T$ of **3**, 4.56 cm^3 K mol^{-1}, is smaller than the spin-only value for isolated $S = 4$ spin. The maximum value of the $\chi_M T$ of **2** demonstrates a higher nuclearity than a cyclic tetranuclear structure.

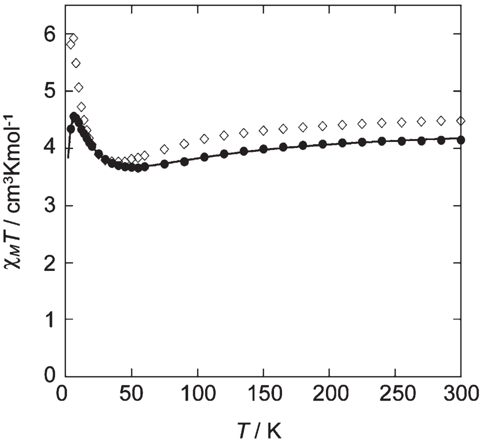

Figure 2. Plots of $\chi_M T$ per Cu–Mn vs temperature for **2**(◇) and **3**(●). The solid line for **3** represents the theoretical curve on the basis of a cyclic tetranuclear structure with the fitting parameters of $g = 1.94$, $J_1 = -13.5\,\text{cm}^{-1}$, $J_2 = -3.3\,\text{cm}^{-1}$, and $zJ' = -0.03\,\text{cm}^{-1}$.

The field dependence of the magnetization was measured up to 5 T at 2 K. Figure 3 shows the experimental results as the plots of $M/N\beta$ vs H at 2 K, where the $M/N\beta$ is the value per Cu–Mn. The variation in the magnetization with H/T for a molecule with an isolated spin multiplet S as the ground state is described by the Brillouin function, i.e., by the expression $M/N\beta = gSB_S(z)$, where $z = g\beta H/kT$ and $B_S(z)$ is the Brillouin function for the S state.[1]

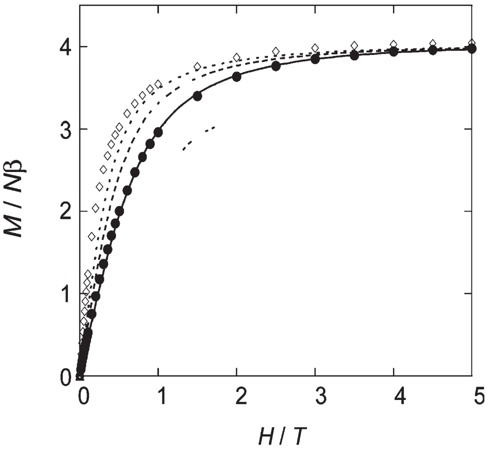

Figure 3. Field dependence of the magnetization at 2 K for **2**(◇) and **3**(●), as the plots of $M/N\beta$ vs H at 2 K, where the $M/N\beta$ is the value per Cu–Mn. The lines represent the theoretical calculated curves for $S = 4$, 6, and 8 spin states from the bottom. The total spin states are produced by antiferromagnetic coupling of the spin system (1/2, 5/2)n ($n = 2$, 3, 4) with cyclic structure.

The magnetization data of **3** are very similar to that of the previously reported cyclic tetranuclear complex [CuL^{1}Mn^{II}(hfac)]$_2$ (**1**).[3c] The magnetization behavior of **3** is well-reproduced by the Brillouin function for $S = 4$ and $g = 1.97$ (the solid line). On the basis of a cyclic tetranuclear structure, the magnetic susceptibility data of **3** were analyzed and the magnetic susceptibility data were well reproduced over the entire temperature range with the fitting parameters of $g = 1.94$, $J_1 = -13.5\,\text{cm}^{-1}$, $J_2 = -3.3\,\text{cm}^{-1}$, and $zJ' = -0.03\,\text{cm}^{-1}$. The temperature-dependent magnetic susceptibility and field-dependent magnetization data showed that compound **3** has an $S = 4$ spin ground state resulting from two antiferromagnetic interactions in the cyclic tetranuclear spin system (1/2, 5/2, 1/2, 5/2). On the other hand, the magnetization of **2** is extremely much abrupt than **3**, and the data are larger than those for independent $S = 4$, 6, and 8 spins. Both the temperature-dependent magnetic susceptibility and field-dependent magnetization indicate an infinite liner chain structure, in which Cu^{II} and Mn^{II} ions are alternately arrayed.

References and Notes

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4 [CuL^{2}Mn(hfac)] (**2**). A methanolic solution (30 mL) of Na[CuL^2] (0.200 g, 0.53 mmol) was gently poured into a methanol solution (30 mL) of [Mn(hfac)$_2$(H$_2$O)$_2$] (0.268 g, 0.53 mmol) at ambient temperature. Reddish purple fine needles formed immediately were collected by filtration, washed with methanol and dried under reduced pressure. Yield: 0.259 g (76%). IR (cm^{-1}): $\nu_{C=O}$ 1651; $\nu_{C=N}$ 1602; ν_{CF} 1254–1145. Anal. Calcd for $C_{22}H_{16}N_2O_6F_6$CuMn: C, 41.49; H, 2.53; N, 4.40%. Found: C, 41.57; H, 2.46; N, 4.26%. [CuL^{3}Mn(hfac)]$_2$ (**3**). This complex was prepared by the same method as for **2** using Na[CuL^3] instead of Na[CuL^2]. Reddish violet fine plates were obtained. Yield: 0.225 g (83%). IR (cm^{-1}): $\nu_{C=O}$ 1650; $\nu_{C=N}$ 1602; ν_{CF} 1251–1152. Anal. Calcd for $C_{23}H_{18}N_2O_7F_6$CuMn: C, 41.42; H, 2.72; N, 4.20%. Found: C, 41.45; H, 2.50; N, 4.22%.

5 The temperature-dependent magnetic susceptibilities and field-dependent magnetization were measured with an MPMS-5S SQUID susceptometer (Quantum Design, Inc.). The calibrations were performed with palladium. Corrections for diamagnetism were applied using Pascal's constants.

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