A Tetranuclear 3d−4f Single Molecule Magnet: [Cu^{II}LTb^{III}(hfac)$_2$]$_2$

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Single molecule magnets (SMMs)[1] have attracted special attention in the past decade, because each individual molecule of SMM can function as a nanoscale magnet. SMM exhibits not only the classical property of a magnet, but also straddles the classical/quantum interface such as the quantum tunneling of magnetization. Since the first discovery of SMM in the Mn$_{12}$ cluster, SMMs have been found in Mn, Fe, V, and Ni polynuclear complexes.[1,2] It is well known that these SMMs have a large high-spin ground state and a large easy-axis type magnetic anisotropy. The unusual combination of high-spin ground state and magnetic anisotropy gives a magnetic bistable molecule, resulting in a significant barrier to thermally activated magnetization relaxation. The synthetic design has been extensively investigated, and several SMMs have been successfully synthesized. However, the condition for SMM with a high-spin ground state and a magnetic anisotropy is not easily achieved. To establish a new and alternative synthetic design of SMM, we have focused on the polynuclear d−f complexes.[3] In our previous paper,[3b] we reported that a cyclic 3d−4f tetranuclear complex [Cu^{II}LLn^{III}(hfac)$_2$]$_2$, in which the 3d and 4f magnetic ions are alternately arrayed, can be the suitable molecule to achieve a large magnetic moment and a magnetic anisotropy. Although these compounds [Cu^{II}LLn^{III}(hfac)$_2$]$_2$ showed no hysteresis at 2 K, we have examined the possibility of SMM using ac magnetic susceptibility measurements. Among the cyclic 3d−4f tetranuclear compounds, two compounds, [Cu^{II}LTb^{III}(hfac)$_2$]$_2$ and [Cu^{II}LDy^{III}(hfac)$_2$]$_2$, showed the frequency dependence of the out-of-phase signal (χ_M''), which is characteristic of SMM. We now report the new class of SMM.

Compound [Cu^{II}LTb^{III}(hfac)$_2$]$_2$ has been almost quantitatively synthesized by mixing methanolic solutions of K[Cu^{II}L] and Tb^{III}(hfac)$_3$(H$_2$O)$_2$ in a 1:1 mole ratio, where H$_3$L = 1-(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxy-benzylideneamino)-ethane and Hhfac = hexafluoroacetylacetone.[4] As shown in Figure 1, the compound assumes a cyclic Cu$^{II}_2$Tb$^{III}_2$ tetranuclear structure, in which the Cu^{II} and Tb^{III} ions are alternately arrayed.

Figure 2 shows the magnetic behaviors of [Cu^{II}LTb^{III}(hfac)$_2$]$_2$, together with those of [Ni^{II}LTb^{III}(hfac)$_2$]$_2$ as the reference compound consisting of diamagnetic Ni^{II} ion. The $\chi_M T$ value of 23.12 K cm^3 mol^{-1} for [Ni^{II}LTb^{III}(hfac)$_2$]$_2$ is almost constant over the whole temperature range except for a decrease in the lowest temperature region. The reciprocal magnetic susceptibility follows the Curie equation of $1/\chi_M = T/C$. The constant value of 23.12 cm^3 K mol^{-1} and the Curie constant of $C = 23.33$ cm^3 K mol^{-1} are consistent with the value of 23.64 cm^3 K mol^{-1} expected for two independent Tb^{III} (4f^8, $J = 6$, $S = 3$, $L = 3$, $^7F_6$) ions and two diamagnetic Ni^{II} ions. On the other hand, upon lowering the temperature, the $\chi_M T$ value of [Cu^{II}LTb^{III}(hfac)$_2$]$_2$ gradually increases from 26.42 cm^3 K
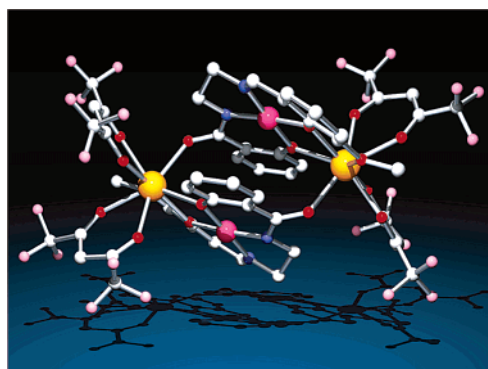
Figure 1. Molecular structure of a cyclic compound [Cu^{II}LTb^{III}(hfac)$_2$]$_2$. Yellow, Tb^{III}; reddish pink, Cu^{II}; red, O; blue, N; white, C; pink, F. The H atoms are omitted.
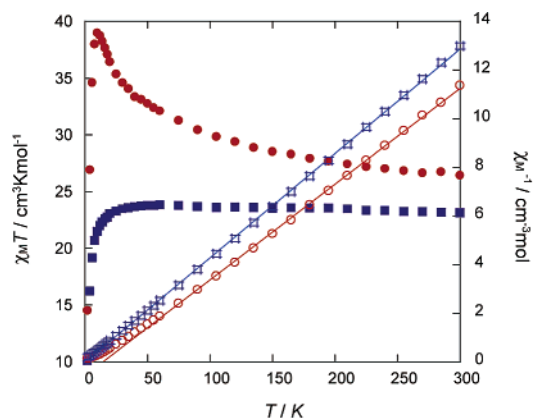
Figure 2. Plots of $\chi_M T$ versus T and $1/\chi_M$ versus T for [Cu^{II}LTb^{III}(hfac)$_2$]$_2$ (red closed circle, red open circle) and [Ni^{II}LTb^{III}(hfac)$_2$]$_2$ (blue closed square, blue open square).

mol^{-1} at 300 K and reaches a maximum value of 38.97 cm^3 K mol^{-1} at 10 K and then decreases, in which the reciprocal magnetic susceptibilities in 50−300 K follow the Curie−Weiss equation of $1/\chi_M = (T − \theta)/C$ with the Curie constant of $C = 25.42$ cm^3 K mol^{-1} and the Weiss constant of $\theta = +14.3$ K. The increase of the $\chi_M T$ value on increasing the temperature and the positive Weiss constant indicate the operation of a ferromagnetic interaction between the Cu^{II} and Tb^{III} ions.

Upon increasing the applied external magnetic field, the magnetization of [Cu^{II}LTb^{III}(hfac)$_2$]$_2$ increases to 17 $N\beta$ at 5 T but does not reach the expected saturation value (9 $N\beta$ for each Tb^{III} ion and 1 $N\beta$ for each Cu^{II} ion). This is due to the crystal field effect on the Tb^{III} ion (4f^8, $J = 6$, $S = 3$, $L = 3$, $^7F_6$) that removes the 13-fold degeneracy of the $^7F_6$ ground state.[5]

As evidenced by the temperature-dependent magnetic susceptibilities and the field-dependent magnetizations, the compound

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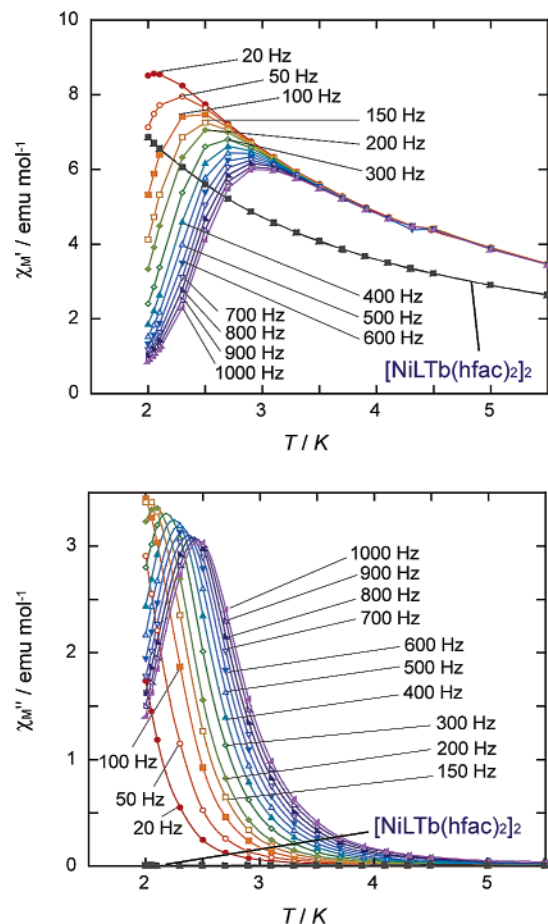
Figure 3. Plots of the in-phase (χ_M') and out-of-phase (χ_M'') signals in ac susceptibility studies versus temperature of [$Cu^{II}LTb^{III}(hfac)_2$]$_2$. The plots for [$Ni^{II}LTb^{III}(hfac)_2$]$_2$ are given.

[$Cu^{II}LTb^{III}(hfac)_2$]$_2$ exhibits a large magnetic moment and a magnetic anisotropy, where the 3d−3d and 4f−4f magnetic interactions can be negligibly small due to the lack of a magnetic mediator between them, the magnetic vectors of the adjacent 3d and 4f ions can be simply assembled due to the 3d−4f ferromagnetic interaction,[3,6] and magnetic anisotropy is introduced by the Tb[III] ion with a first-order orbital angular momentum.[5]

One of the characteristics of a SMM is the observation of an out-of-phase (χ_M'') ac susceptibility signal. The ac measurements were carried out in a 3.0 G ac field oscillating at the indicated frequencies (20−1000 Hz) and with a zero dc field. Figure 3 shows the results of the ac magnetic susceptibility measurements for [$Cu^{II}LTb^{III}(hfac)_2$]$_2$ and [$Ni^{II}LTb^{III}(hfac)_2$]$_2$ as the plots of χ_M' versus T and χ_M'' versus T. For [$Cu^{II}LTb^{III}(hfac)_2$]$_2$, the in-phase $\chi_M'T$ signal shows a frequency-dependent decrease, indicative of the onset of a slow relaxation on the measurement time scale diagnostic of a SMM. This was confirmed by the concomitant appearance of an out-of-phase signal due to the inability of a SMM to rapidly relax at these temperatures to keep up with the oscillating field. The out-of-phase component of the ac susceptibility (χ_M'') shows frequency-dependent peaks. This behavior is indicative of the slow relaxation of the magnetization, which is unusual for a paramagnet without an applied field. The χ_M'' signal has a peak at 2.5 K at a 1000 Hz

ac frequency, where the position of the peak corresponds to the temperature at which the relaxation rate is equal to the ac oscillation frequency. Data obtained by varying the frequency of oscillation of the ac field were fit to the Arrhenius equation ($1/T = k_B/\Delta(\ln(2\pi\nu) + \ln(\tau_0))$) to obtain the energy barrier for the relaxation of the magnetization. The best fitting parameters obtained are $\tau_0 = 2.7 \times 10^{-8}$ s and $\Delta/k_B = 21$ K. It should be noted that no hysteresis was observed at 2 K, due to the estimated blocking temperature of $T_B = 1.2$ K.

Very recently, Ishikawa et al. has shown that a SMM behavior can occur in an isolated Tb[III] complex with phthalocyanine.[7] We have examined whether the slow relaxation of the magnetization really arises from the ferromagnetic coupled tetranuclear complex [$Cu^{II}LTb^{III}(hfac)_2$]$_2$ or is just intrinsic to the Tb[III] centers by studying the analogous complex [$Ni^{II}LTb^{III}(hfac)_2$]$_2$ with diamagnetic Ni[II] in place of Cu[II]. As shown in Figure 3, [$Ni^{II}LTb^{III}(hfac)_2$]$_2$ showed no frequency-dependent signals of χ_M' and χ_M'' in the same temperature range, demonstrating that the present SMM behavior is not intrinsic to the Tb[III] centers.

Compound [$Cu^{II}LDy^{III}(hfac)_2$]$_2$ exhibits a frequency dependence of the χ_M'' signal consistent with SMM behavior, although no maximum was observed down to 2 K. The reference compound [$Ni^{II}LDy^{III}(hfac)_2$]$_2$ showed no frequency-dependent signals of χ_M' and χ_M''.

We reported that two cyclic 3d−4f tetranuclear compounds [$Cu^{II}LLn^{III}(hfac)_2$]$_2$ (Ln = Tb, Dy) assume a SMM behavior. The present study demonstrates that the synthesis of the d−f polynuclear molecule is a very promising approach to SMMs. There are several advantages: (1) the d−f polynuclear molecule can be easily synthesized by the assembly reaction of the d-component exhibiting a donor coordination ability and the f-component exhibiting an acceptor coordination ability, (2) the high-spin ground state can be generated by a smaller number of metal ions than the d polynuclear complex, and (3) the molecular magnetic anisotropy is easily derived from the f-component.

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