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Oximate-Bridged Trinuclear Dy−Cu−Dy Complex Behaving as a Single-Molecule Magnet and Its Mechanistic Investigation

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Discrete oligonuclear complexes with bridging ligands are of increasing interest for the development of synthetic magnets since single-molecule magnets (SMMs) were discovered.[1] Recently, SMM behavior has been observed in 4f−3d heterometallic complexes,[2−5] such as $[\mathrm{Tb^{III}_2Cu^{II}_2}]$,[2] as well as even in mononuclear $\mathrm{Tb^{III}}$, $\mathrm{Dy^{III}}$, and $\mathrm{Ho^{III}}$ phthalocyanates.[6] Single-chain magnets have been derived from $[\mathrm{Mn^{III}_2Ni^{II}}]_n$ coordination polymers using the $\mathrm{N{-}O^-}$ bridge of pyridine-2-aldoximate.[7] We have also developed various oximates to novel 4f−3d bridges[8,9] and will report here the observation of magnetization steps with hysteresis in $[\mathrm{Dy^{III}_2Cu^{II}}]$ containing di-2-pyridyl ketoximate (dpk$^-$). Although quantum tunneling of magnetization (QTM) has been well studied in the 3d metal SMMs,[1] mechanisms for SMM behavior found in 4f-3d-metal-based complexes are unknown. We will provide for the first time a theoretical framework to understand the QTM of 4f−3d clusters in terms of a simple Ising-like model with well-defined exchange coupling between 4f−3d metal ions.

The trinuclear core was successfully constructed from the precursors $[\mathrm{Cu(dpk)_2}]$ and $[\mathrm{Dy(hfac)_3}]$ without scrambling ligands or metal ions (hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate). Figure 1 shows the exactly linear array Dy1−Cu1−Dy1*, where the oximate $\mathrm{N{-}O^-}$ group bridges Dy1 and Cu1. The Dy1 ion is octacoordinate as expected; three hfac ligands remained from the starting material $[\mathrm{Dy(hfac)_3}]$. The Cu1 ion has a square planar configuration, being coordinated by four nitrogen atoms in five-membered chelate rings. The core structure is similar to that of $[\{\mathrm{Dy(hfac)_3}\}_2\{\mathrm{Ni(dpk)_2(py)_2}\}]$ except for the additional axial ligands in the nickel analogue.[9]

The temperature dependence of the $\chi_{\mathrm{mol}}T$ for a randomly oriented polycrystalline sample of $[\mathrm{Dy_2Cu}]$ (Figure S1) showed the value of 26.0 cm^3 K mol^{-1} at 250 K, which agrees with the theoretical value of 28.7 cm^3 K mol^{-1} expected from uncoupled spins with $J = S + L = 15/2$, $g = 4/3$ for $\mathrm{Dy^{III}}$ and $S = 1/2$, $g = 2$ for $\mathrm{Cu^{II}}$. The $\chi_{\mathrm{mol}}T$ value gradually decreased on cooling, reached a minimum of 19.8 cm^3 K mol^{-1} at 4.5 K, and finally exhibited a very slight upsurge below 4.5 K. The upsurge suggests that the magnitude of magnetic interactions between the Dy and Cu ions is much smaller than an order of 1 K. The $M-H$ measurements on a single crystal of $[\mathrm{Dy_2Cu}]$ at 1.8 K revealed that the magnetization of the *a*-axis (easy axis) saturated more rapidly than that of the *c*-axis (hard axis). No hysteresis was observed for temperatures above 1.8 K.

Shown in Figure 2 is the frequency dependence of χ_{ac}' and χ_{ac}'' for $[\mathrm{Dy_2Cu}]$. On cooling, an increase of χ_{ac}'' was found together with a decrease of χ_{ac}'.[10] When we plotted the χ_{ac}'' data against χ_{ac}' at 8.0 K according to the Cole−Cole analysis[11] (the inset of Figure 2b), a semicircle was clearly drawn, indicating a single relaxation process.

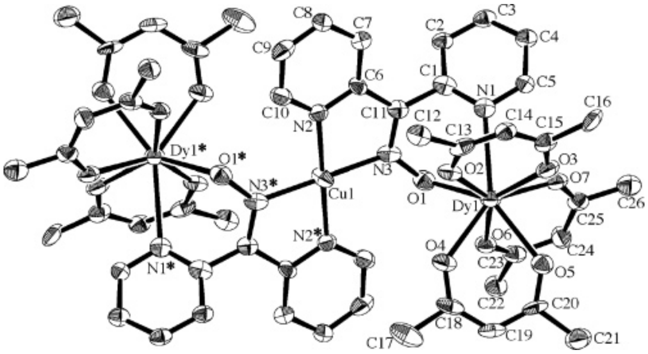

Figure 1. Ortep drawing of $[\{\mathrm{Dy(hfac)_3}\}_2\{\mathrm{Cu(dpk)_2}\}]$ with thermal ellipsoids at the 50% probability level. Hydrogen and fluorine atoms are omitted. The symmetry operation code of $*$ is given by $-x$, $-y$, $-z$.

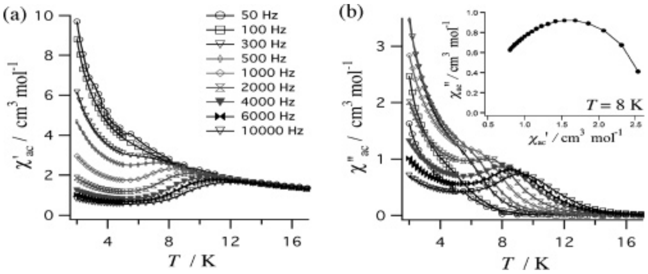

Figure 2. Frequency and temperature dependence of the ac magnetic susceptibility for $[\mathrm{Dy_2Cu_1}]$. (a) χ_{ac}' (in-phase part). (b) χ_{ac}'' (out-of-phase part). Inset shows the Cole−Cole diagram at 8.0 K.

The relaxation rate ($1/\tau$) is equal to the frequency of the applied ac field ($2\pi\nu$) at the temperature of the maximum of χ_{ac}''. We can analyze the energy barrier (Δ) of the magnetization reorientation based on an Arrhenius-type equation,[7] $\ln(2\pi\nu) = -\ln(\tau_0) - \Delta/k_{\mathrm{B}}T$, giving $\Delta/k_{\mathrm{B}} = 47(4)$ K and $\tau_0 = 1.1(5) \times 10^{-7}$ s. The Δ value obtained here is much larger than that of $[\mathrm{Tb_2Cu_2}]$ behaving as a 4f−3d SMM.[2] The Arrhenius analysis on $[\mathrm{Dy_2Cu}]$ also suggests that the blocking under the limited conditions of $\nu = 10^{-5}$ Hz (i.e., τ becomes hours) will take place below 1.8 K.

The SMM behavior of $[\mathrm{Dy_2Cu}]$ could not be attributed solely to Dy single-ion properties, such as the phthalocyanine Dy salt.[6] We confirmed that the starting material $[\mathrm{Dy(hfac)_3(H_2O)_2}]$ showed practically no frequency dependence of the χ_{ac}''. A stronger coupling of $\mathrm{Cu^{II}}$ to $\mathrm{Dy^{III}}$ ions than that of the $\mathrm{Ni^{II}}$ analogue[9] could be responsible for the slower relaxation.

To corroborate a SMM behavior, we performed magnetization measurements below 1.8 K using a pulsed field.[12] Figure 3a shows the results of a polycrystalline sample of $[\mathrm{Dy_2Cu}]$ at 1.5 and 0.5 K in a full-cycle sweeping field (the left inset). The distinct feature is the observation of hysteresis loops and magnetization steps. The

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10.1021/ja057183f CCC: $33.50 © 2006 American Chemical Society

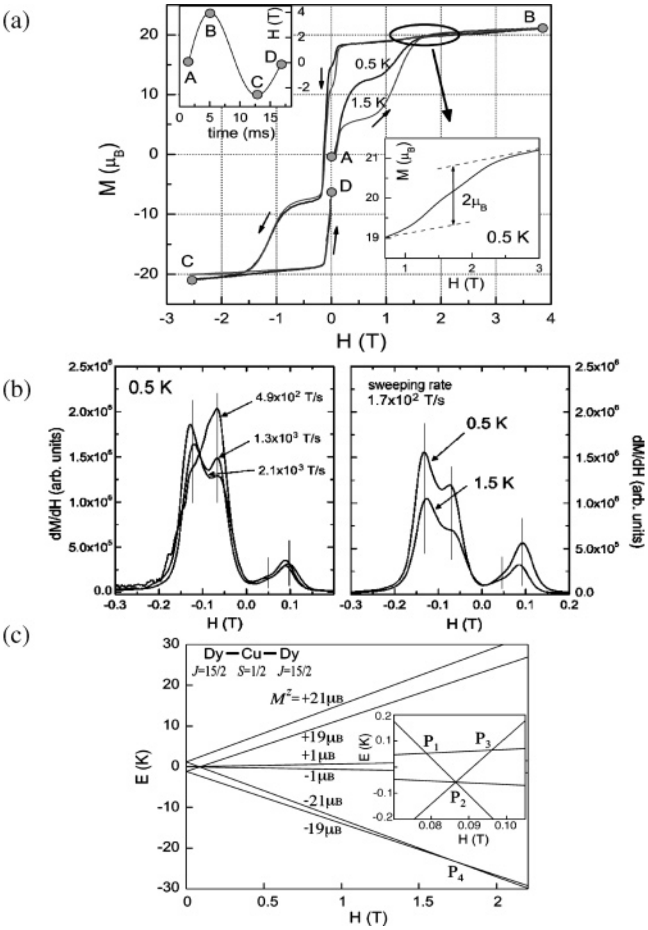

Figure 3. (a) Hysteresis curves for [Dy_2Cu] measured at 1.5 and 0.5 K. The field sweeping rate was 1.7×10^3 T s^{-1}. Left inset: a sweeping field as a function of time. Right inset: a zoom of a higher magnetic field showing a magnetization jump by 2 μ_B. (b) Differential magnetization curves as a function of a sweeping rate (left) and temperature (right). (c) Energy levels of [Dy_2Cu] in a ground-state manifold.

detailed study of the derivative of the magnetization (Figure 3b) shows no appreciable field-sweeping rate or temperature dependence of the step positions. This finding gives direct evidence that the magnetization is due to an adiabatic change of magnetization rather than due to thermal relaxation. Noticeably, the big steps occur at very low fields of 0.05 and 0.095 T, while the 2 μ_B jump at a relatively higher field around 1.7 T (the right inset of Figure 3a). The latter corresponds to a spin flip of the Cu ion, confirming the presence of antiferromagnetic superexchange interaction between the Cu and Dy ions. The former is related to the reorientation of the Dy ions possessing a large magnetic moment of 10 μ_B. To unveil the full aspect of the observed QTM, we should determine an energy diagram.

The experimental values of the $\chi_{\rm mol}T$ and saturation magnetization indicate that a ground state of the Dy ions is given by the maximal value of $|J^z| = 15/2$, being separated from the first excited-state group typically by more than a few hundred kelvin even for a single Dy ion.[6] For a description of a low-temperature magnetic behavior, thus it suffices to consider a coupling between a ground state of Dy ion, $J^z = 15/2$, and $S = 1/2$ of Cu ion.[13] Owing to a strong axial anisotropy of Dy ion, an Ising interaction, J_I, between Dy and Cu ions including the Zeeman term can be a minimal Hamiltonian:

$$\hat{H} = -J_{\rm I}\,(\hat{J}_1^z + \hat{J}_3^z)\cdot\hat{S}_2^z + \mu_B H^z\,(g_{\rm Dy}J_1^z + g_{\rm Cu}S_2^z + g_{\rm Dy}J_3^z)$$

Note that J_I is a unique adjustable parameter in this model. By comparing the observed magnetization to the theoretical estimation, we obtain $J_I/k_B = -0.155$ K and derive an energy level diagram (Figure 3c). At a zero field, the ground state consists of a doubly degenerated $|M^z| = 19\ \mu_B$ state (Dy↑−Cu↓−Dy↑). The first excited state is a 4-fold degenerated $|M^z| = 1\ \mu_B$ state (Dy↑−Cu↑−Dy↓ for example), and the second exited state is doubly degenerated ($|M^z| = 21\ \mu_B$; Dy↑−Cu↑−Dy↑). At a finite field, we find four level crossings, P_1(0.078 T), P_2(0.086 T), P_3(0.096 T), and P_4(1.7 T) as shown in Figure 3c. The 2 μ_B jump corresponds to P_4, while the two steps at 0.05 and 0.095 T in Figure 3b are assigned to the P_2 and P_3 points, which cross a ground state. The point P_1 is missing since most of the spins are in a ground state at 0.5 K, with the energy gap of $(15/2)J_I/k_B = 1.16$ K between the ground and excited states. The reasonable agreement between the experimental and theoretical values justifies the validity of our proposed model, assuming that the magnetization along the easy axis mainly contributes to the polycrystalline data. In the up sweep, the magnetization jump around 1.2 T, which has no counterpart in the level crossing diagram, depends strongly on the field sweeping rate and temperature. This behavior is attributed to relaxation of thermally excited spins to the ground state.

In summary, we have shown straightforward experimental evidence for QTM in the 4f-metal-based [Dy_2Cu] SMM and derived the energy level structure on the basis of an Ising model together with Dy−Cu exchange coupling. Remarkably, the dimethylglyoximate-bridged [$Dy^{III}{}_4Cu^{II}$] complex exhibited a QTM at 0.5 K and a similar model can be applied.[14] The 4f−3d combination may afford various SMM families and will provide a deep understanding to the mechanism of QTMs.

Acknowledgment. This work was partly supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Figure S1, experimental details, and the CIF file of [Dy_2Cu_1]. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA057183F