Single-Molecule Magnets

The Effect of the f–f Interaction on the Dynamic Magnetism of a Coupled $4f^8$ System in a Dinuclear Terbium Complex with Phthalocyanines**

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The observation of long magnetic relaxation times of bis(phthalocyaninato)terbium at high temperatures has led to a new category of magnets at the single-molecular level that are based on lanthanide complexes.[1] The relaxation times determined by alternating current (ac) magnetic susceptibility measurements for the Tb^{III} complex $[Pc_2Tb]^-$ (Pc denotes the dianion of phthalocyanine) are, for example, 0.16 ms at 40 K and 1.6 s at 8 K.[2] These temperatures are considerably higher than those reported for the transition-metal clusters known as "single-molecule magnets" (SMMs).[8,9] The long relaxation times of the Tb–Pc complex at high temperatures result from the characteristic ligand-field-splitting pattern of the $J=6$ ground multiplet of the Tb^{III} ion with a $4f^8$ electronic configuration.[3–7] The ligand-field potential of pseudo-D_{4d} symmetry made by the two Pc macrocycles lifts the 13-fold degeneracy and yields a situation in which the lowest substates with $J_z = \pm 6$ are greatly separated (by about 400 cm^{-1}) from the rest of the substates.[8,9] This splitting pattern causes a low transition rate between the lowest substates and thus slow relaxation is observed.

The phthalocyaninato ligand is known to form other sandwich-type complexes that are composed of three Pc ligands and two lanthanide ions. These complexes are often referred to as triple deckers. The lanthanide ions are placed along the fourfold symmetry axis with a metal–metal interatomic distance of about 3.6 Å. If Tb^{III} ions are placed at the lanthanide sites, the resultant complex can be viewed as a system in which two $4f^8$ systems, each having relaxation times of the order of a millisecond to a second, are coupled by an f–f interaction.[10] Such a system is in fact hard to find and, to the best of our knowledge, has not been reported with any other lanthanide complex. In this sense, the bis-Tb complex provides us with a rare opportunity to carry out experimental studies on the dynamic magnetism of coupled 4f electronic systems.

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[**] We thank Prof. Dr. Shin-ya Koshihara, Department of Materials Science, Tokyo Institute of Technology, for granting machine time on the magnetometer, and Dr. Tadahiko Ishikawa for assistance with data collection. This work was supported by a Grant-in-Aid for Science Research No. 15550046 from the Ministry of Education, Science, Sports, and Culture of Japan.

DOI: 10.1002/ange.200461546

Herein we present the first report on the dynamic magnetism of a coupled $4f^8$ system. The effect of the f–f interaction on the temperature and frequency dependence of the ac magnetic susceptibility will be clarified by the comparison of experimental data for isostructural bis-Tb and mono-Tb complexes.

Concerning the nature of the f–f interaction in the triple-decker Pc complexes, Ishikawa et al. previously reported the analysis of the NMR spectra and the temperature dependence of the static magnetic susceptibilities of the dinuclear complexes of heavy lanthanides (Tb, Dy, Ho, Er, Tm, and Yb) and concluded that the interaction was essentially dominated by the magnetic dipolar term in all six cases.[10–12] In the case of the bis-Tb complex, the magnetic dipolar interaction between the Tb ions leads to a parallel or ferromagnetic arrangement of magnetic moments at low temperatures.[11]

We have prepared a homodinuclear complex [Tb, Tb] (Figure 1) and two heterodinuclear complexes [Y, Tb] and [Tb, Y], in which one Tb ion is replaced by a diamagnetic $\mathrm{Y^{III}}$ center. The compounds were synthesized by using a previously reported method.[10,11] The ac magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL magnetometer.

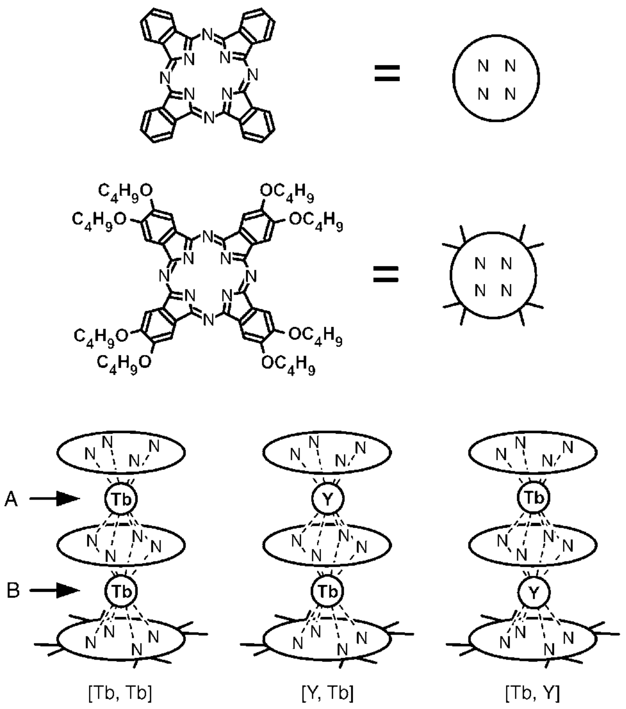

Figure 1. Structures of [Tb, Tb], [Y, Tb], and [Tb, Y]. A and B indicate the two different metal coordination environments, see text.

Figure 2 shows the temperature dependence of ac susceptibilities of the three complexes diluted in a diamagnetic [Y, Y] matrix with a concentration of 5%. The mono-Tb complexes exhibit a decrease in χ_M'/χ_M values and nonzero χ_M''/χ_M values as the temperature is lowered. The χ_M''/χ_M peaks for the 997-Hz field are observed at 7 K and 18 K for the [Y, Tb] and [Tb, Y] complexes, respectively. The difference in the temperature ranges in which the relaxation phenomena are observed reflects the difference in the ligand-field potential between the two lanthanide sites.

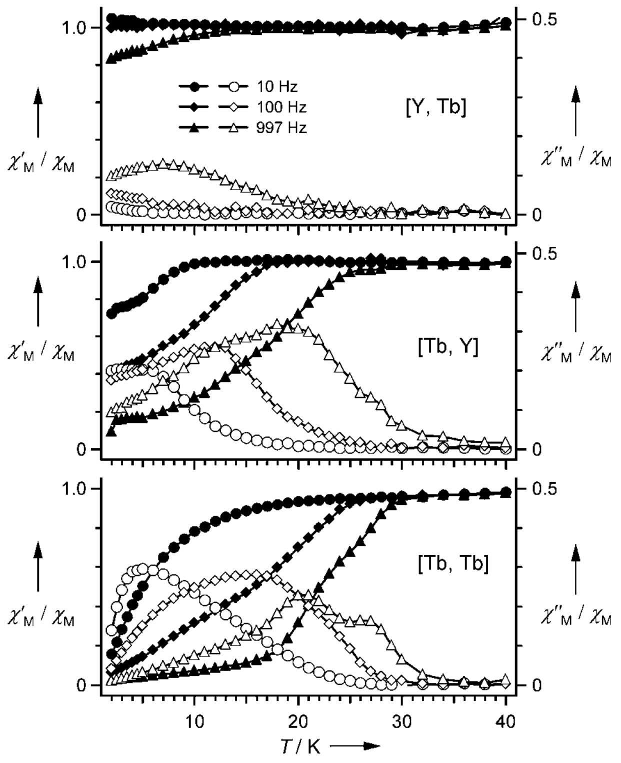

Figure 2. Plots of χ_M'/χ_M (closed symbols) and χ_M''/χ_M (open symbols) against temperature T, in which χ_M' is the in-phase ac magnetic susceptibility, χ_M'' is the out-of-phase ac magnetic susceptibility, and χ_M is the dc molar magnetic susceptibility, for a powder sample of [Y, Tb] (top), [Tb, Y] (middle), and [Tb, Tb] (bottom).

The bis-Tb complex [Tb, Tb] shows the relaxation phenomenon at a higher temperature range than those of the mono-Tb complexes (Figure 2, bottom). This result means that the f–f interaction increases the magnetization relaxation time of [Tb, Tb]. Even more interestingly, the χ_M''/χ_M plot for the 997-Hz field contains two peaks at 27 K and 20 K. It appears that the χ_M''/χ_M peaks of mono-Tb complexes are shifted to higher temperatures in the bis-Tb complex. We have proved experimentally that this is in fact the case.

Figure 3 shows the ac susceptibility data taken under a nonzero dc magnetic field. As the dc field increases, the χ_M''/χ_M peaks of the [Y, Tb] and [Tb, Y] complexes shift to higher temperatures. The shift reaches its maximum at a dc field of about 2000 Oe. In contrast, in the [Tb, Tb] complex the positions of the two χ_M''/χ_M peaks do not change. Most importantly, the positions of the shifted peaks of both the mono-Tb complexes almost coincide with the two peaks of the bis-Tb complex. This result clearly indicates that the two peaks of [Tb, Tb] at 27 and 20 K actually correspond to the $\mathrm{Tb^{III}}$ ions at sites A and B (see Figure 1), respectively.

The shift of the χ_M''/χ_M peak position of the mono-Tb complexes with an increase in the dc field should be closely related to the difference of the ground-state eigenfunctions that are between the zero-field and highfield limits. As previously reported, the lowest substates of the mono-Tb

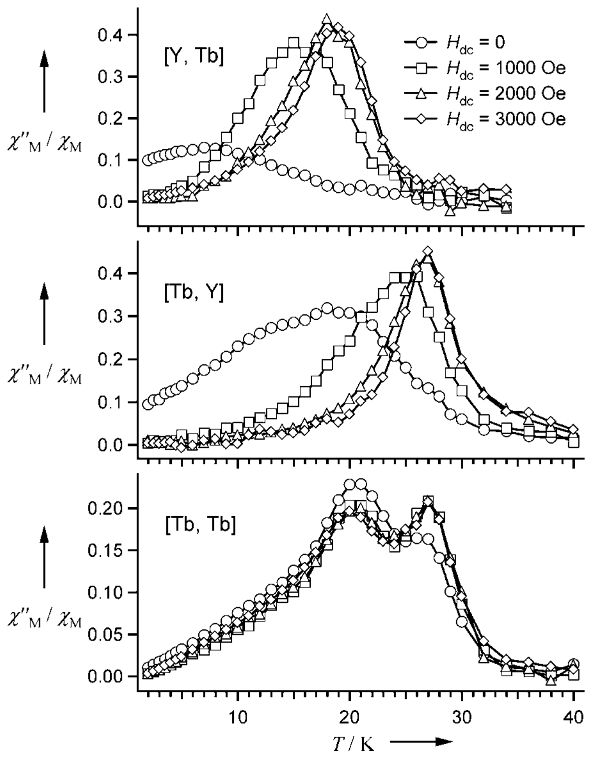

Figure 3. Plots of χ_M''/χ_M against temperature T of [Y, Tb] (top), [Tb, Y] (middle), and [Tb, Tb] (bottom) measured in a 5G ac magnetic field of 997 Hz with dc field H_{dc} of indicated magnitudes.

complexes are described predominantly by the two functions $|+6\rangle$ and $|-6\rangle$,[10,11] which correspond to the eigenfunctions at the highfield limit. In the absence of a magnetic field, the zero field eigenfunctions are $\{|+6\rangle \pm |-6\rangle\}/2^{1/2}$,[10,11] due to the presence of the nonzero off-diagonal matrix elements of the ligand-field potential, which indirectly couples $|+6\rangle$ and $|-6\rangle$.[13,14] As the magnetic field increases, the eigenfunctions vary as $\{\cos\theta|+6\rangle - \sin\theta|-6\rangle\}$ and $\{\sin\theta|+6\rangle + \cos\theta|-6\rangle\}$ with θ changing from $\pi/4$ to zero. The relaxation time to reach the equilibrium state is accordingly changed from the zero-field to the highfield limit.

In the case of the [Tb, Tb] complex, the eigenfunctions are expressed by the products of two basis functions, namely $\Phi^A\Phi^B$, in which A and B refer to the two Tb ions. The appropriate choice for the basis function Φ^X (X = A or B) is either $|+6\rangle$ or $|-6\rangle$, even in the zero-field case, because the magnetic dipolar interaction between the two Tb ions gives different diagonal energies to $|+6\rangle^A\ |J_z\rangle^B$ and $|-6\rangle^A\ |J_z\rangle^B$ (and to $|J_z\rangle^A\ |+6\rangle^B$ and $|J_z\rangle^A\ |-6\rangle^B$), in which J_z is either 6 or -6.[11,15] Consequently, the admixture of $|+6\rangle$ and $|-6\rangle$ that is seen in the mono-Tb case does not occur in the bis-Tb case. This explains the small dc-field dependence on the ac susceptibility observed for the [Tb, Tb] complex.

In conclusion, we have obtained the following information on the dynamical magnetism of the coupled $4f^8$ system. 1) Under a zero dc field, the magnetic relaxation time of the bis-Tb complex at a given temperature increases compared to the mono-Tb complexes. 2) The double-peak appearance of the χ_M''/χ_M plot of the [Tb, Tb] complex indicates that the relaxation processes in the two $4f^8$ systems occur somewhat independently of each other, at least in the temperature range above 20 K, although the two systems are certainly coupled by an f–f interaction. 3) The two χ_M''/χ_M peaks of [Tb, Tb] at 27 and 20 K correspond to the relaxations that occur at sites A and B, respectively. 4) The upward temperature shift of the χ_M''/χ_M peaks observed for the mono-Tb complexes corresponds to the resolution of the admixing of $|+6\rangle$ and $|-6\rangle$ states. In contrast, the f–f interaction in the [Tb, Tb] complex prevents the admixture of $|+6\rangle^X$ and $|-6\rangle^X$ states (X is either A or B) at the zero-field limit, which results in the greatly reduced dc-field dependence of the ac susceptibility.

Received: August 5, 2004

Keywords: lanthanides · magnetic properties · sandwich complexes · single-molecule magnets · terbium

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