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Article

Static Magnetic-Field-Induced Phase Lag in the Magnetization Response of Tris(dipicolinato)lanthanides

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Alternating-current (ac) magnetic susceptibility measurements for tris(dipicolinato) complexes with a trivalent heavy lanthanide ion, $[N(C_2H_5)_4]_3[Ln(dipic)_3]\cdot nH_2O$ (dipic = pyridine-2,6-dicarboxylate; Ln = Tb, Dy, Ho, Er, Tm, or Yb) are reported. While none of the six complexes showed a magnetization lag from the ac magnetic field of $10–10^3$ Hz above 1.8 K, the Dy, Er, and Yb complexes with odd numbers of 4f electrons exhibited the magnetization lag in a static magnetic field. This phenomenon is explained to be caused by the elimination of a fast relaxation path, which is only effective for the Kramers doublet ground states in near zero field. At higher static fields, the remaining paths such as Orbach and/or direct processes govern the dynamics of the two-level systems comprised of spin-up and spin-down states. The non-Kramers complexes were found to have a nondegenerate ground state with large energy gaps from higher states, which is consistent with their fast magnetization relaxation.

Introduction

The possibility of constructing single-molecule magnets (SMMs)[1−5] using a single lanthanide ion has been demonstrated in recent studies on phthalocyaninatolanthanide complexes having a double-decker or triple-decker structure.[6] A significant difference between the well-established 3d

metal-cluster SMMs[1−5,7−11] and the lanthanide single-ionic SMMs resides in how the magnetic anisotropy and preferred direction of the magnetic moment are achieved. In the 3d cluster SMM cases such as $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]^{n-}$ (n = 0, 1, 2; x = 3, 4)[1−5,7,8] and $[Mn^{IV}Mn^{III}_4O_3X]$,[9−11] the easy-axis-type magnetic anisotropy, which is represented by the negative zero-field-splitting constant D, is caused by the magnetic interactions among high-spin 3d metal ions in a molecule. In the lanthanide single-ionic SMM cases, on the other hand, such anisotropy is given by the ligand field (LF) in which the lanthanide ion is placed.

The lanthanide single-ionic SMMs reported to date are those with tetragonal LFs due to the tetradentate phthalocyanine macrocycles. Out of six heavy lanthanide phthalo-

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 (1) Christou, G.; Gatteschi, D.; Hendrichson, D. N.; Sessoli, R. *MRS Bull.* **2000**, *25* (11), 66.
 (2) (a) Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrichson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804. (b) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141.
 (3) (a) Barbara, B.; Wernsdorfer, W.; Sampaio, L. C.; Park, J. G.; Paulsen, C.; Novak, M. A.; Ferré, R.; Mailly, D.; Sessoli, R.; Caneschi, A.; Hasselbach, K.; Benoit, A.; Thomas, L. *J. Magn. Magn. Mater.* **1995**, *140*, 1825. (b) Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. *Nature* **1996**, *383*, 145.
 (4) (a) Friedman, J. R.; Sarachik, M. P.; Tejada, J.; Ziolo, R. *Phys. Rev. Lett.* **1996**, *76*, 3830. (b) Tejada, J.; Ziolo, R. F.; Zhang, X. X. *Chem. Mater.* **1996**, *8*, 1784. (c) Hernández, J. M.; Zhang, X. X.; Luis, F.; Bartolomé, J.; Tejada, J.; Ziolo, R. *Europhys. Lett.* **1996**, *35*, 31.
 (5) (a) Eppley, H. J.; Tsai, H.-L.; de Vries, N.; Folting, K.; Christou, G.; Hendrichson, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 301. (b) Aubin, S. M. J.; Spagna, S.; Eppley, H. J.; Sager, R. E.; Christou, G.; Hendrichson, D. N. *Chem. Commun.* **1998**, 803. (c) Aubin, S. M. J.; Sun, Z.; Pardi, L.; Krzystek, J.; Folting, K.; Brunel, L.-C.; Rheingold, A. L.; Christou, G.; Hendrichson, D. N. *Inorg. Chem.* **1999**, *38*, 5329.

 (6) (a) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. *J. Am. Chem. Soc.* **2003**, *125*, 8684. (b) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. *J. Phys. Chem. B* **2004**, *108*, 8684. (c) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. *Inorg. Chem.* **2004**, *43*, 5498.
 (7) Soler, M.; Chandra, S. K.; Ruiz, D.; Davidson, E. R.; Hendrichson, D. N.; Christou, G. *Chem. Commun.* **2000**, 2417.
 (8) Boskovic, C.; Pink, M.; Huffman, J. C.; Hendrichson, D. N.; Christou, G. *J. Am. Chem. Soc.* **2001**, *123*, 9914.
 (9) Aubin, S. M. J.; Wemple, M. W.; Adams, D. M.; Tsai, H.-L.; Christou, G.; Hendrichson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 7746.
(10) Aubin, S. M. J.; Dilley, N. R.; Pardi, L.; Krzystek, J.; Wemple, M. W.; Brunel, L. C.; Maple, M. B.; Christou, G.; Hendrichson, D. N. *J. Am. Chem. Soc.* **1998**, *120*, 4991.
(11) Andres, H.; Basler, R.; Gudel, H.-U.; Aromi, G.; Christou, G.; Buttner, H.; Ruffle, B. *J. Am. Chem. Soc.* **2000**, *122*, 12469.

Chart 1. $[Ln(dipic)_3]^{3-}$ (Ln = Tb, Dy, Ho, Er, Tm, or Yb)
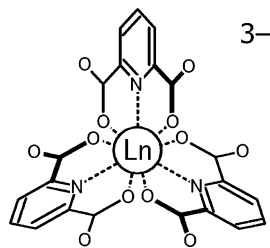
cyaninato complexes, Tb and Dy complexes showed the magnetization lag from the alternating-current (ac) magnetic field, which is a general characteristic of the SMMs, in the absence of a direct-current (dc) field. Arrhenius analysis of the temperature dependence of the relaxation time showed that the main relaxation path is the two-phonon Orbach process above 25 K for Pc_2Tb^- and above 3 K for Pc_2Dy^-.[6b]

Recently, magnetic susceptibility measurements in the sub-Kelvin temperature range revealed that Pc_2Tb^- and Pc_2Dy^- exhibit staircaselike structures in magnetization hysteresis curves.[12] Similar structures are also observed for Pc_2Ho^-.[13] Such staircaselike structures were first discovered for the Mn_{12} systems[3,4] and have been shown to be caused by the quantum tunneling of magnetization (QTM).[3,4,14] The quantum nature of the 3d metal-cluster SMMs is also manifested by temperature-independent relaxation[15] and quantum phase interference.[16] The discovery of these phenomena led to potential applications of the SMMs for quantum computing.[17] The presence of the additional relaxation path through QTM in the lanthanide counterparts accounts for the sharp drops of magnetization near zero field observed in the hysteresis loops of the powder sample of Pc_2Tb^- and Pc_2Dy^- [6b] and the dc-field dependence of the relaxation time observed for Tb–Y hetero-dinuclear, Pc triple-decker complexes.[18]

The finding of SMM behaviors in Pc lanthanide complexes naturally leads to the question of whether such behaviors are observed in lanthanide complexes of different categories. Setting aside such a question, investigation on complexes with different symmetries and different LFs is evidently crucial for a deeper understanding of the dynamical magnetism of lanthanide complexes in general, as well as for the development of new lanthanide SMMs.

In this paper, we report ac susceptibility measurements on tris(dipicolinato)lanthanides $[Ln(dipic)_3]^{3-}$ (Chart 1; dipic
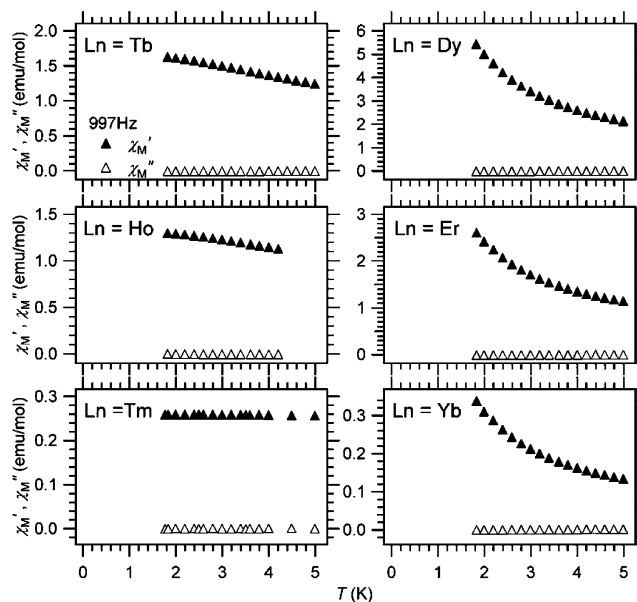

Figure 1. Plot of χ_m' (closed markers) and χ_m'' (open markers) against temperature T, where χ_m' and χ_m'' are in-phase ac and out-of-phase ac magnetic susceptibilities, respectively, for the powder sample of $[N(C_2H_5)_4]_3$-$[Ln(dipic)_3]\cdot nH_2O$. The measurements were performed in a 5 Oe ac magnetic field oscillating at 997 Hz with the absence of the dc component.

= pyridine-2,6-dicarboxylate; Ln = Tb, Dy, Ho, Er, Tm, or Yb) possessing a trigonal (D_3) symmetry. We show here that this representative class of lanthanide complexes exhibits remarkable dc magnetic field dependences of ac susceptibilities, which is observed only for Kramers systems with odd numbers of 4f electrons. The reason for this unusual dependence is discussed based on the sublevel structures of the ground-state multiplets of the six lanthanide complexes estimated by the simultaneous fitting method previously reported.

Experimental Section

The samples of $[N(C_2H_5)_4]_3[Ln(dipic)_3]\cdot nH_2O$ (Ln = Tb, Dy, Ho, Er, Tm, Yb; $n = 4$ for Ln = Tb, Dy; $n = 3$ for Ln = Ho, Er; $n = 2$ for Ln = Tm, Yb) were prepared by the literature method[19] with minor modifications. The ac magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL magnetometer. The microcrystalline powder samples were dispersed in eicosane to prevent potential torquing of the magnetically anisotropic samples. The dc magnetic susceptibility measurements were carried out on a Quantum Design MPMS-5 SQUID (superconducting quantum interference device) magnetometer. As the correction for the diamagnetic susceptibility contribution in each the sample, corresponding experimental data for $[N(C_2H_5)_4]_3[Y(dipic)_3]\cdot 3H_2O$ was used. ^1H NMR spectra of the complexes were measured in a CD_3OD solution with $(CH_3)_4Si$ as that internal standard on a JEOL Lambda-400 NMR spectrometer.

Results and Discussion

ac Magnetic Susceptibility Measurements. Figure 1 shows the temperature dependence of the ac magnetic

(12) Ishikawa, N.; Sugita, M.; Wernsdorfer, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 2931.

(13) Ishikawa, N.; Sugita, M.; Wernsdorfer, W. *J. Am. Chem. Soc.* **2003**, *125*, 8684.

(14) Giraud, R.; Wernsdorfer, W.; Tkachuk, A. M.; Mailly, D.; Barbara, B. *Phys. Rev. Lett.* **2001**, *87*, 057203.

(15) (a) Aubin, S. M. J.; Dilley, N. R.; Wemple, M. W.; Maple, M. B.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1998**, *120*, 839. (b) Aubin, S. M. J.; Dilley, N. R.; Pardi, L.; Krzystek, J.; Wemple, M. W.; Brunel, L.-C.; Maple, M. B.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1998**, *120*, 4991. (c) Sangregorio, C.; Ohm, T.; Paulsen, C.; Sessoli, R.; Gatteschi, D. *Phys. Rev. Lett.* **1997**, *78*, 4645. (d) Brechin, E. K.; Boskovic, C.; Wernsdorfer, W.; Yoo, J.; Yamaguchi, A.; SaVudo, E. C.; Concolino, T. R.; Rheingold, A. L.; Ishimoto, H.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **2002**, *124*, 9710. (e) Soler, M.; Rumberger, E.; Folting, K.; Hendrickson, D. N.; Christou, G. *Polyhedron* **2001**, *20*, 1365. (f) Andres, H.; Basler, R.; Blake, A. J.; Cadiou, C.; Chaboussant, G.; Grant, C. M.; GJdel, H.-U.; Murrie, M.; Parsons, S.; Paulsen, C.; Semadini, F.; Villar, V.; Wernsdorfer, W.; Winpenny, R. E. P. *Chem.—Eur. J.* **2002**, *8*, 4867.

(16) Wernsdorfer, W.; Sessoli, R. *Science* **1999**, *284*, 133.

(17) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *410*, 789.

(18) Ishikawa, N.; Otsuka, S.; Kaizu, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 731.

(19) Brayshaw, P. A.; Bünzli, J.-C. G.; Froidevaux, P.; Harrowfield, J. M.; Kim, Y.; Sobolev, A. N. *Inorg. Chem.* **1995**, *34*, 2068.
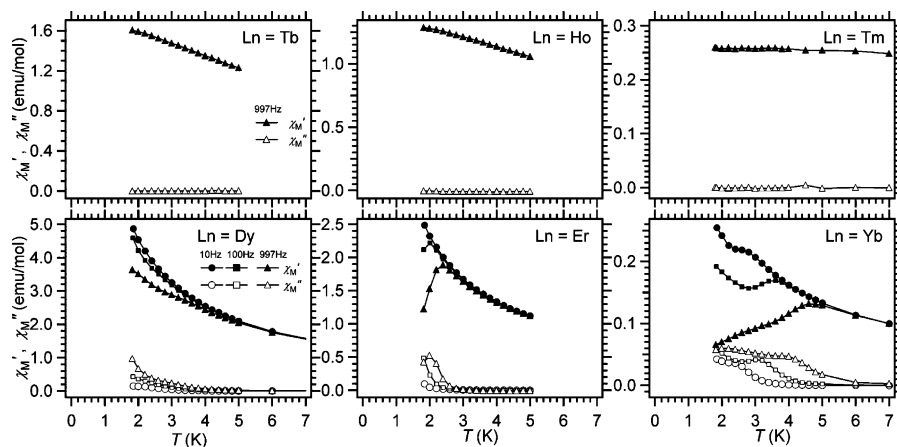
Figure 2. Plot of χ_m' (closed markers with solid lines) and χ_m'' (open markers with solid lines) against temperature T, where χ_m' and χ_m'' are in-phase ac and out-of-phase ac magnetic susceptibilities, respectively, for the powder sample of $[N(C_2H_5)_4]_3[Ln(dipic)_3] \cdot nH_2O$, measured with a 5 Oe ac magnetic field oscillating at the indicated frequencies in a dc field of 1000 Oe.

susceptibilities of the powder samples of $[N(C_2H_5)_4]_3[Ln-(dipic)_3] \cdot nH_2O$ measured in zero dc magnetic field. The six complexes showed no out-of-phase component of ac magnetic susceptibilities χ_m'' above 1.8 K, with the ac magnetic field oscillating at $f = 997$ Hz, while in-phase components χ_m' increased monotonically with lowering of the temperature. This result indicates that the magnetization relaxation time (τ) of these complexes is much shorter than the reciprocal of the angular frequency of the ac field [$\omega^{-1} = (2\pi f)^{-1}$], and the magnetic moments completely follow the ac magnetic field.

In the presence of a static magnetic field, remarkable changes were observed. Figure 2 shows the results of ac susceptibility measurements performed in a dc magnetic field of 1000 Oe. Out of the six complexes, Dy, Er, and Yb complexes show a significant decrease in χ_m' from the corresponding values in zero dc field because lowering T, as well as χ_m'', peaks or raises the temperature ranges depending on the ac frequency, indicating that the response of the magnetic moment to the ac magnetic field is becoming slower. The Yb complex showed χ_m'' peaks at 2.4, 3.0, and 4.0 K with frequencies of 10, 100, and 997 Hz, respectively. The χ_m'' peak was observed for the Er complex at 2.0 K with a frequency of 997 Hz. In the Dy case, an increase of χ_m'' with decreasing T was observed for all ac frequencies.

Such behaviors are not observed for the Tb, Ho, and Tm complexes: ac susceptibility measurements in the dc field gave essentially the same data as those obtained with the absence of the dc field.

These results show an intriguing correlation: the three complexes showing ac magnetization lag in a static magnetic field are of Kramers systems with odd numbers of 4f electrons, and those showing no lag are of non-Kramers systems with even 4f electrons.

Determination of the Ground-State Multiplet Substructures. With the hope to gain an understanding of the above-mentioned experimental results, we have attempted a determination of the sublevel structures of the ground-state multiplet of the six tris(dipicolinato)lanthanide complexes with the "simultaneous determination"[20] of LF parameters

of the isostructural set of complexes. In the previous papers,[20] we demonstrated that the multiplet substructures of a series of lanthanide complexes having isomorphic structures can be determined by finding the set of LF parameters that simultaneously reproduces the ^1H NMR paramagnetic shifts and the magnetic susceptibilities measured at various temperatures. We have determined a set of LF parameters that gives the least-squares fit to the products of the dc molar magnetic susceptibilities and temperatures ($\chi_m T$) at 2, 4, 8, 15, 30, 70, and 150 K and the paramagnetic shift ($\Delta\delta$) values of the para proton of the six complexes at 189, 199, 210, 221, 231, 242, 252, 263, 273, 283, 294, and 303 K. In the present work, $\Delta\delta$ is defined as the deviation of a chemical shift value δ of a paramagnetic species from that of diamagnetic $[N(C_2H_5)_4]_3[Y(dipic)_3] \cdot 3H_2O$.

The total angular momentum of the ground state in the trivalent heavy lanthanide ions with $(4f)^8 - (4f)^{13}$ configurations is $J = L + S$. Each J state has $2J + 1$ sublevels in the ground-state multiplet. The Hamiltonian of a system under an external magnetic field is

$$\hat{H} = \mu_B(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{H} + \mathbf{F}$$

The first term of the right-hand side is the Zeeman effect. The orbital and spin angular momentum matrices, $\mathbf{L}$ and $\mathbf{S}$, are those reconstructed so that the basis for the matrix elements is $|J, J_z\rangle$.

The second term is the LF interaction, which is expressed by the operator equivalent.[21] Following the notation by Abragam and Bleaney,[22] the LF term belonging to the D_3 point group is written as

$$\mathbf{F} = A_2^0\langle r^2\rangle\alpha\mathbf{O}_2^0 + A_4^0\langle r^4\rangle\beta\mathbf{O}_4^0 + A_4^3\langle r^4\rangle\beta\mathbf{O}_4^3 + A_6^0\langle r^6\rangle\gamma\mathbf{O}_6^0 +$$
$$A_6^3\langle r^6\rangle\gamma\mathbf{O}_6^3 + A_6^6\langle r^6\rangle\gamma\mathbf{O}_6^6$$

The coefficients $A_k^q\langle r^k\rangle$ are the parameters to be determined.

(20) (a) Ishikawa, N. *J. Phys. Chem. A* **2003**, *107* (30), 5831. (b) Ishikawa, N.; Iino, T.; Kaizu, Y. *J. Phys. Chem. A* **2002**, *106*, 9543. (c) Ishikawa, N.; Iino, T.; Kaizu, Y. *J. Am. Chem. Soc.* **2002**, *124*, 11440. (d) Ishikawa, N.; Sugita, M.; Okubo, T.; Tanaka, N.; Iino, T.; Kaizu, Y. *Inorg. Chem.* **2003**, *42*, 2440.
(21) Stevens, K. W. H. *Proc. Phys. Soc. A* **1952**, *65*, 209.

The $\mathbf{O}_k^q$ matrices are polynomials of the total angular momentum matrices $\mathbf{J}^2$, $\mathbf{J}_z$, $\mathbf{J}_-$, and $\mathbf{J}_+$, and their definitions are described in ref 22. The z axis is chosen to coincide with the C_3 axis. The coefficients α, β, and γ are the constants tabulated by Stevens.[21] In the present paper, we employed an assumption that each parameter is constant throughout the heavy lanthanide series.

A set of $A_k^q\langle r^k\rangle$ coefficients and a finite external field determine the wave functions and magnetic moments of all of the substates. The magnetization of an ensemble at a certain temperature is obtained considering Boltzmann distribution. The magnetic susceptibility per molecule is given by dividing the magnetization by the magnetic field applied. Thus, three principal values, χ_{xx}, χ_{yy}, and χ_{zz}, are obtained.

The observed molar magnetic susceptibility χ_m of a powder sample is

$$\chi_m = N_A\bar{\chi}$$

$$\bar{\chi} = \frac{1}{3}(\chi_{xx} + \chi_{yy} + \chi_{zz})$$

where N_A is Avogadro's number. Because the paramagnetic center of each molecule is placed in a LF of C_3 symmetry, the following relation is held:

$$\chi_{xx} = \chi_{yy}$$

The dipolar contribution in the ^{1}H NMR paramagnetic shift $\Delta\delta$ is written as

$$\Delta\delta = \frac{\Delta\nu}{\nu} = \frac{(3\cos^2\theta - 1)}{2R^3}(\chi_{zz} - \bar{\chi})$$

where ν is the resonance frequency in the reference diamagnetic molecule, $\Delta\nu$ is the change in the frequency in the paramagnetic molecule, R is the distance between the paramagnetic center and the proton to be considered, and θ is the corresponding azimuth.[23]

We have employed the $\Delta\delta$ value of the proton at the para position with respect to the nitrogen atom for the fitting calculation because the θ value for the para position is fixed at 90° whereas that for the proton at the meta position may be varied significantly from case to case.

The values of R were estimated by adding the differences of the ionic radii between the trivalent lanthanide ions and Y^{3+} to the value of $R = 6.41$ Å, which was calculated for $[Y(dipic)_3]^{3-}$ with density functional theory (DFT) with a B3LYP/LANL2DZ model using the X-ray crystal structure of $Cs_3[Eu_2(dipic)]$[19] as the starting values of the DFT optimization to the D_3-symmetrical structure.

Table 1 presents the LF parameter set that gives the best fit to the $\Delta\delta$ vs T plots as shown in Figure 3 and to the $\chi_m T$ vs T plots as in Figure 4. The two figures show that the thus-estimated LF parameter set reproduces both the ^{1}H NMR and SQUID data with a good accuracy.

(22) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance*; Clarendon Press: Oxford, U.K., 1970.
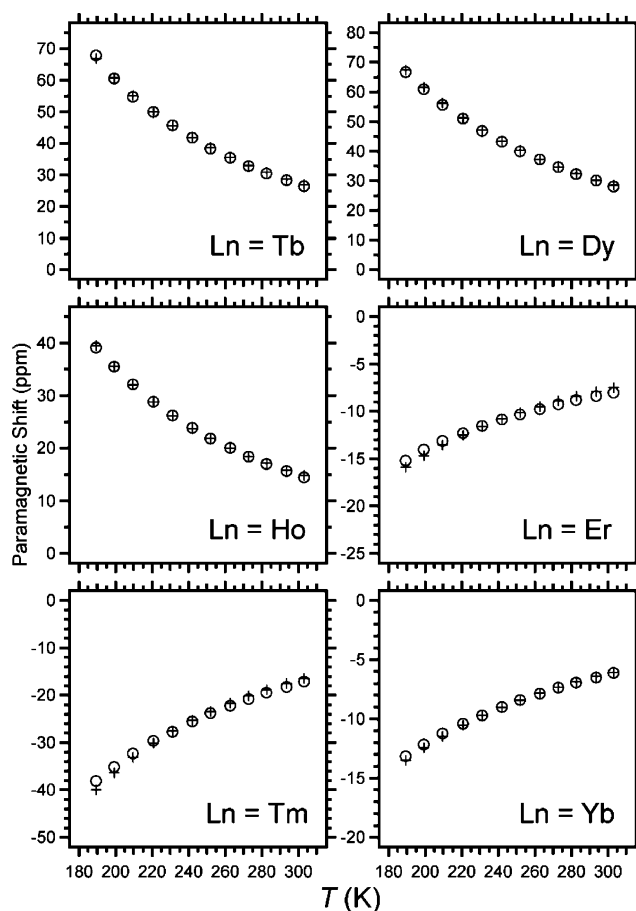(23) Bleaney, B. *J. Magn. Reson.* **1972**, *8*, 91.

Figure 3. Plot of the theoretical (crosses) and experimental (circles) values of the paramagnetic shift $\Delta\delta$ for the para proton on the dipic ligands in $[N(C_2H_5)_4]_3[Ln(dipic)_3]\cdot n H_2O$ against temperature.

Table 1. Estimated LF Parameters $A_2^0\langle r^2\rangle$, $A_4^0\langle r^4\rangle$, $A_4^3\langle r^4\rangle$, $A_6^0\langle r^6\rangle$, $A_6^3\langle r^6\rangle$, and $A_6^6\langle r^6\rangle$ of $[N(C_2H_5)_4]_3[Ln(dipic)_3]\cdot n H_2O$ (Ln = Tb, Dy, Ho, Er, Tm, or Yb)

$A_2^0\langle r^2\rangle$	$A_4^0\langle r^4\rangle$	$A_4^3\langle r^4\rangle$	$A_6^0\langle r^6\rangle$	$A_6^3\langle r^6\rangle$	$A_6^6\langle r^6\rangle$
-142 cm^{-1}	-41 cm^{-1}	575 cm^{-1}	-14 cm^{-1}	419 cm^{-1}	-514 cm^{-1}

Correlation between dc-Field Dependence of the Magnetization Lag and the Parity of the Numbers of 4f Electrons. The wave functions of the lowest substates of these complexes obtained with the above LF parameters are shown in Table 2. The three Kramers systems (Dy, Er, and Yb complexes) have doubly degenerate ground states whose primal components are the spin states with large or moderate $|J_z|$ values. On the other hand, those of the non-Kramers complexes are nondegenerate singlets belonging to the A_1 representation in the D_3 point group. The energy level diagrams for the ground-state multiplets given by the LF parameters are shown in Figure 5. The diagrams show that in each case the lowest substate is well separated (by more than 10 cm^{-1}) from the higher substates and therefore is predominantly occupied in the temperature range below 7 K, in which the ac susceptibility measurements have been performed.

Figure 6 illustrates how the ground states are modified by an application of a static magnetic field. In the Kramers cases, the two components of the ground-state doublet form a crossing at $H = 0$. It is known that a small transverse

Table 2. Wave Functions of the Lowest Substates of the Ground-State Multiplets of $[N(C_2H_5)_4]_3[Ln(dipic)_3] \cdot nH_2O$ (Ln = Tb, Dy, Ho, Er, Tm, or Yb) Obtained Using the Estimated LF Parameters Shown in Table 1

Ln	Γ^a	wave function				
Tb	A_1	$0.94\,|0\rangle$	$-0.23\,|+3\rangle$	$+0.23\,|-3\rangle$	$-0.03\,|+6\rangle$	$-0.03\,|-6\rangle$
Dy	E'	$0.75\,|+7/2\rangle$	$+0.64\,|-5/2\rangle$	$+0.10\,|+1/2\rangle$	$-0.08\,|-11/2\rangle$	
	E'	$0.75\,|-7/2\rangle$	$+0.64\,|+5/2\rangle$	$-0.10\,|-1/2\rangle$	$+0.08\,|+11/2\rangle$	
Ho	A_1	$0.58\,|0\rangle$	$-0.43\,|+3\rangle$	$+0.43\,|-3\rangle$	$-0.37\,|+6\rangle$	$-0.37\,|-6\rangle$
Er	E'	$0.71\,|+15/2\rangle$	$-0.57|+9/2\rangle$	$-0.35\,|-3/2\rangle$	$+0.11\,|-9/2\rangle$	$+0.09\,|-3/2\rangle$
	E'	$0.71\,|-15/2\rangle$	$+0.57\,|-9/2\rangle$	$+0.35\,|+3/2\rangle$	$+0.11\,|+9/2\rangle$	$+0.09\,|+3/2\rangle$
Tm	A_1	$0.57\,|6\rangle$	$+0.57\,|-6\rangle$	$-0.41\,|0\rangle$	$+0.29\,|+3\rangle$	$-0.29\,|-3\rangle$
Yb	E'	$0.70\,|+5/2\rangle$	$+0.69\,|-7/2\rangle$	$+0.14\,|-1/2\rangle$		
	E'	$0.70\,|-5/2\rangle$	$+0.69\,|+7/2\rangle$	$-0.14\,|+1/2\rangle$		

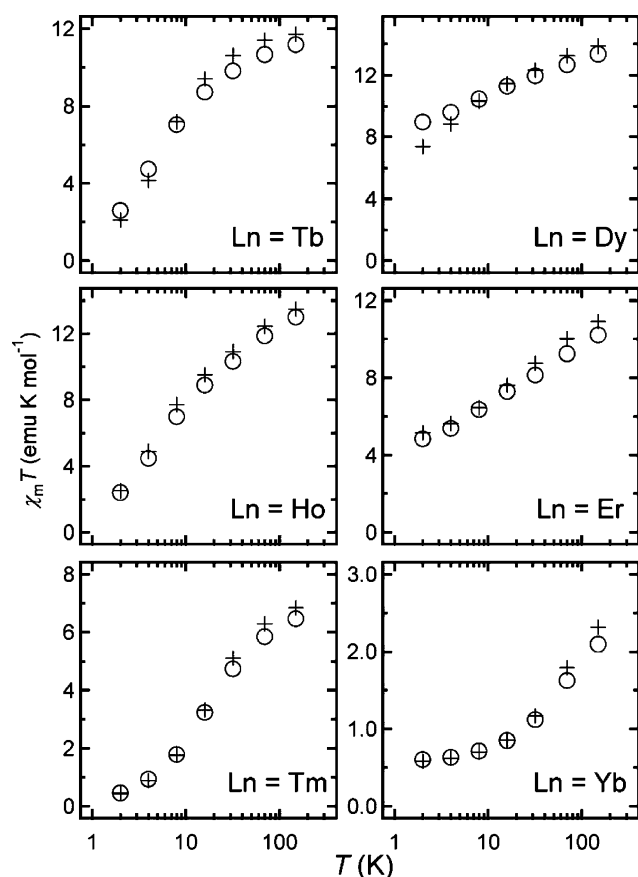[a] Representation in the D_3 point group.

Figure 4. Plot of the theoretical (crosses) and experimental (circles) values of $\chi_m T$ against temperature, where $\chi_m T$ is the product of the dc molar magnetic susceptibility and the temperature for the powder sample of $[N(C_2H_5)_4]_3[Ln(dipic)_3] \cdot nH_2O$.

Figure 5. Energy diagram for the ground-state multiplets of $[Ln(dipic)_3]^{3-}$ (Ln = Tb, Dy, Ho, Er, Tm, or Yb). The characters next to the substates correspond to the representation in the D_3 point group for the wave function of each substate.

magnetic field created by the fluctuation of the internal magnetic field can couple the components of a doublet state, giving rise to an avoided crossing. In such a case, magnetization relaxation can occur through the QTM mechanism. Upon application of a static field, the possibility of the magnetic relaxation by this process disappears because the two states are not degenerate any longer. The relaxation of such a two-level system in a static field is governed by the next fastest path, such as Orbach or direct processes.[22]

The dc-field dependence of the magnetic relaxation time due to the additional relaxation path of the QTM mechanism was first reported for 3d metal-cluster systems by Barbara et al.[3] and Tejada et al.[4] Magnetization measurements for a single crystal of Mn_{12} SMM or oriented crystallites made
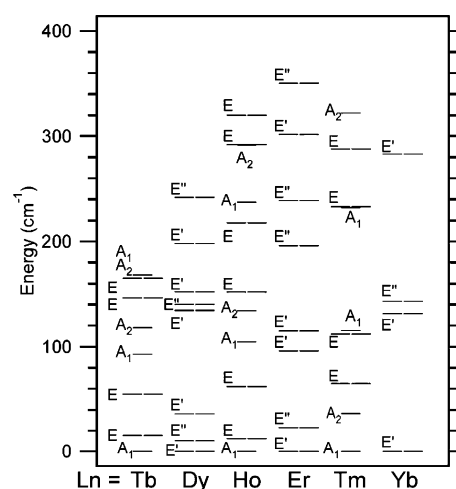
from powdered Mn_{12} samples have shown the existence of the distinct "staircase" structures in the hysteresis loops. At these special values of the dc magnetic field, where the energies of different collective spin states of the manganese clusters coincide, relaxation is strongly enhanced. Magnetization decay measurements have indeed clearly demonstrated that relaxation time greatly decreases at these values of the dc field, where the steps are observed in the hysteresis loops.[3,4] A similar phenomenon has been observed for the Fe_8 cluster SMM.[24] An increase of the relaxation time by application of nonzero dc field from the value at zero dc field has also been shown by ac susceptibility measurements for 3d metal SMMs with Mn_{12},[4c] $[Mn^{IV}Mn^{III}_3O_3Cl]^{6+}$,[10] or $[V_4O_2]^{8+}$ core.[25]

In the non-Kramers systems, on the other hand, the ground state is nondegenerate. The energy gaps between the ground state and the lowest excited state are estimated at more than $10\ cm^{-1}$ for the three cases. This indicates that the argument for the two-level systems does not apply for these systems. The situation is essentially unaltered by the presence of the static magnetic field, as shown in Figure 6.

The lifting of the 2-fold degeneracy in the lowest substate of the non-Kramers systems is due to the presence of the

(24) Sangregorio, C.; Ohm, T.; Paulsen, C.; Sessoli, R.; Gatteschi, D. *Phys. Rev. Lett.* **1997**, *78*, 4645.
(25) Castro, S. L.; Sun, Z.; Grant, C. M.; Bollinger, J. C.; Hendrichson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1998**, *120*, 2997.
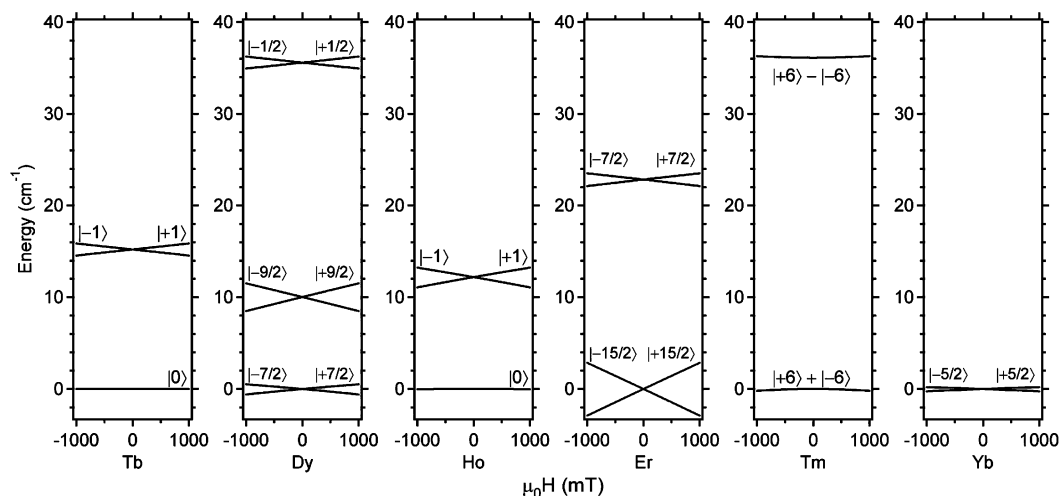
Figure 6. Part of the energy diagram as a function of the longitudinal magnetic field for the ground-state multiplets with the LF parameters for $[Ln(dipic)_3]^{3-}$ (Ln = Tb, Dy, Ho, Er, Tm, or Yb) shown in Table 1. The primal component of the wave function for each substate is presented on each line.

nonzero off-diagonal matrix elements of LF potential, which occur with the nonzero parameters $A_4^3\langle r^4\rangle$, $A_6^3\langle r^6\rangle$, and $A_6^6\langle r^6\rangle$. In the lanthanide complex chemistry in general, it is often assumed that off-diagonal terms in the LF potential are negligible and only the quadratic term $A_2^0\langle r^2\rangle\alpha\mathbf{O}_2^0$ is sufficient to be considered. However, if one employs such an approximation, only degenerate substates are concluded, and therefore it is not possible to explain the observed field dependence in the ac susceptibilities. Thus, inclusion of the off-diagonal terms is mandatory to explain the present experimental results.

The $[Yb(dipic)_3]^{3-}$ complex shows the slow relaxation in the highest temperature range among the three Kramers systems, meaning that the Yb complex possesses the long magnetic relaxation times at higher T. The J_z values of the primal components of the ground-state doublet do not have a clear correlation with the length of the relaxation time, as seen in Figure 6. A distinct feature of the Yb complex from the other two is the large energy gap between the ground-state doublet and the first excited state. If the main relaxation path in high dc field is the Orbach process; the large energy gap gives a long relaxation time to the Yb complex. The Orbach mechanism is defined as a two-phonon process, which involves a phonon absorption to excite the spin system to a higher state at an energy Δ above the lowest sublevels, followed by the emission of another phonon with the energy $\Delta + h\nu$ or $\Delta - h\nu$, where $h\nu$ corresponds to the Zeeman splitting of the ground-state doublet.[22] If this process is dominant, τ^{-1} is proportional to $\Delta^3\{\exp(\Delta/kT) - 1\}^{-1}$.[22] In the above numerical simulation, the energy gap was estimated at about 130 cm^{-1} for $[Yb(dipic)_3]^{3-}$, whereas the corresponding gaps of the Dy and Er complexes are 1 order of magnitude smaller (Figure 6). This large difference in the energy gaps explains the distinctively slower relaxation of the Yb complex than the other two.

Last, we point out that a similar dc-field-dependent slow magnetization relaxation was reported in a family of lanthanide transition-metal complexes $[Gd(bpy)(H_2O)_4M(CN)_6]\cdot$

$1.5H_2O$ (bpy = 2,2′-bipyridinato; M = Fe^{3+}, Co^{3+})[26] and analogue compounds $[Nd(bpym)(H_2O)_4M(CN)_6]\cdot3H_2O$ (bpym = 2,2′-bipyrimidinato; M = Fe^{3+}, Co^{3+}).[27] In these compounds, the lanthanide ions and 3d metal ions are linked by cyano ligands, forming three-dimensional network structures in which neighboring magnetic ions can be magnetically coupled. In such systems, as the authors concluded, the slow magnetization relaxation is achieved by the interactions between the magnetic ions. This is a completely different situation from the present case, in which the lanthanide complexes are not chemically bound to each other. In this sense, the seemingly same behaviors in the linked 4f−3d systems and the present discrete 4f systems must be categorized separately and must not to be confounded to one another.

Conclusion

While the six tris(dipicolinato)lanthanides do not exhibit slow magnetic relaxation in zero dc field, the three Kramers systems, $[Dy(dipic)_3]^{3-}$, $[Er(dipic)_3]^{3-}$, and $[Yb(dipic)_3]^{3-}$, acquire long magnetic relaxation times in the presence of a dc magnetic field. The correlation between the parity of the number of 4f electrons and the dc-field dependence is accounted for by the sublevel structure of the multiplet and, more specifically, by the degeneracy of the ground state of each complex. The acquisition of the long relaxation times results from the disappearance of the QTM relaxation path upon application of the dc field.

(26) Gao, S.; Su, G.; Yi, T.; Ma, B.-Q. *Phys. Rev. B* **2001**, *63*, 054431.
(27) Ma, B.-Q.; Gao, S.; Su, G.; Xu, G.-X. *Angew. Chem., Int. Ed.* **2001**, *40*, 434.