

Slow Magnetic Relaxation in Lanthanide Complexes with Chelating Nitronyl Nitroxide Radical

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Two rare-earth radical complexes $[\text{Ln}(\text{hfac})_3\text{NIT-2Py}] \cdot 0.5\text{C}_7\text{H}_{16}$ [$\text{Ln} = \text{Tb}$ (**1**), Dy (**2**)] have been synthesized and characterized structurally as well as magnetically. Both complexes are isomorphous, in which the NIT-2Py radical is coordinated to the Ln^{III} ion in a chelating manner. Magnetic studies reveal that complex **1** shows a frequency-dependent, alternating-current magnetic susceptibility typical of a single-molecule magnet, whereas slow magnetic relaxation is observed in **2** under an applied direct-current field.

The design and synthesis of single-molecule magnets (SMMs) have attracted special attention in the molecular-based magnetic material field.¹ SMMs opened a new page in modern coordination chemistry with the promise of a revolution in data storage and processing.² The origin of the SMM behavior is an easy-axis magnetic anisotropy ($D < 0$), which causes the formation of an energy barrier that prevents the reversal of the molecular magnetization and causes slow magnetic relaxation at low temperature. The important factors leading to the SMM behavior derive from the combined effects of a large-spin multiplicity of the ground state and a large magnetic anisotropy of the Ising type (easy-axis). A large number of complexes displaying SMM behavior have been reported since the discovery in the early 1990s of the first SMM, Mn_{12} acetate.³ More recently, heteropolymetallic

complexes have been intensely studied,⁴ and in the continuous research, rare-earth ions, especially heavy lanthanide ions such as terbium(III) and dysprosium(III),⁵ have been widely used to design SMMs because they have a large angular momentum in the ground multiplet state, which is derived from the strong spin–orbit coupling. Moreover, these metal ions are assumed to have a large Ising-type magnetic anisotropy depending on the geometry and the negative charge distribution of the coordination geometry.⁶ To date, a number of 3d–4f metal clusters⁷ as well as pure 4f metal systems^{8,9} have been observed, displaying frequency-dependent behavior. In these systems, the large magnetic anisotropy of lanthanides means that 3d–4f or 4f metal-based SMMs could possess larger energy barriers provided the magnetic principal axes of these ions are properly oriented. It is worth noting that even mononuclear complexes of lanthanides can show strong slow relaxation behavior,⁹ which may indicate that the ligand (or electric) field is another important player in controlling the magnetic anisotropy of lanthanide-based SMMs.^{5c} Compared to the 3d–4f SMMs, far fewer radical lanthanide SMMs have been reported. So far, only four radical lanthanide SMMs have been reported. They include three cyclic four-spin dimers^{10a–c} from Gatteschi's group and ours and a mononuclear three-spin complex ($[\text{Tb}(\text{hfac})_3(\text{NITPhOEt})_2]$).^{10d} In this Communication, we report two mononuclear Ln^{III} radical complexes using a chelating nitronyl nitroxide radical, $[\text{Ln}(\text{hfac})_3\text{NIT-2Py}] \cdot 0.5\text{C}_7\text{H}_{16}$ [$\text{Ln} = \text{Tb}$ (**1**),

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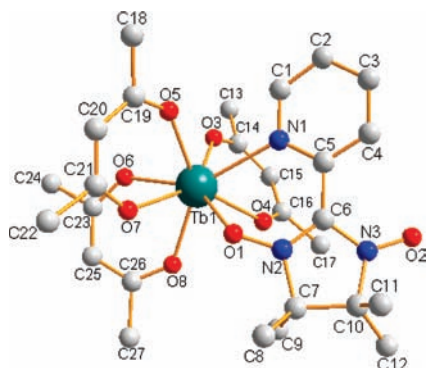


Figure 1. Molecular structure of **1**. Fluorine, heptane, and hydrogen atoms are not shown for the sake of clarity.

Dy (**2**); hfac = hexafluoroacetylacetonate; NIT-2Py = 2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide]. Complex **1** exhibits the frequency-dependent alternating-current (ac) susceptibility, while complex **2** shows slow magnetic relaxation under a static magnetic field. To the best of our knowledge, they are the first examples of mononuclear lanthanides coordinated by a chelating nitronyl nitroxide radical exhibiting slow magnetic relaxation resembling SMM behavior.

Complexes **1** and **2** were synthesized by mixing $\text{Ln}(\text{hfac})_3 \cdot 2\text{H}_2\text{O}$ and NIT-2Py (see the Supporting Information, SI).

Single-crystal X-ray diffraction analyses reveal that the two complexes are isostructural and consist of a $\text{Ln}(\text{hfac})_3\text{-NIT-2Py}$ moiety and half of an *n*-heptane solvent molecule (Figures 1 and S1 in the SI). The Ln^{III} ion is eight-coordinated by six oxygen atoms from three bidentate hfac ligands and one oxygen atom and one nitrogen atom from one bidentate NIT-2Py ligand. The NIT-2Py radical coordinates to the Ln^{III} ion with the oxygen atom of a N–O group and the nitrogen atom of the pyridine ring in a chelating manner. The Ln–N and Ln–O(nitroxide group) bond lengths are 2.598(8) and 2.317(2) Å for **1** and 2.586(6) and 2.306(6) Å for **2**, which are comparable to those reported in other lanthanide–pyridine-substituted radical complexes.^{10,11} The dihedral angles formed by the pyridyl ring and nitroxide groups (O1–N2–C6–N3–O2) of the radical ligands are 26.8 and 26.7° for **1** and **2**, respectively. Figures S2 and S3 (in the SI) show the packing diagrams of complexes **1** and **2**. The shortest distances between $\text{Ln} \cdots \text{Ln}$ are 9.273 and 9.261 Å for **1** and **2**, respectively. The shortest contacts between the uncoordinated NO groups in complexes **1** and **2** are 7.793 and 7.78 Å, respectively, implying that the complex molecules are well isolated.

The susceptibilities of complexes **1** and **2** were measured in the 2–300 K range under the applied magnetic field of 1000 G, and the magnetic behaviors are shown in Figure 2. At room

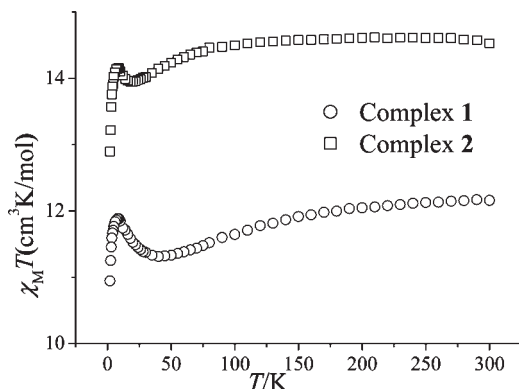


Figure 2. Plots of $\chi_M T$ versus T for complexes **1** and **2**.

temperature, the values of $\chi_M T$ are 12.16 $\text{cm}^3 \text{K mol}^{-1}$ for **1** and 14.56 $\text{cm}^3 \text{K mol}^{-1}$ for **2**, in agreement with the expected values^{5c} (12.20 and 14.55 $\text{cm}^3 \text{K mol}^{-1}$) for one uncoupled Ln^{III} ion (${}^7\text{F}_6$ and $g = 3/2$ for the Tb^{III} ion and ${}^6\text{H}_{15/2}$ and $g = 4/3$ for the Dy^{III} ion) and one organic radical ($S = 1/2$). For complex **1**, upon cooling, the $\chi_M T$ value gradually decreases to reach a value of 11.31 $\text{cm}^3 \text{K mol}^{-1}$ at 40 K, below 40 K; $\chi_M T$ rapidly increases to a maximum value of 11.88 $\text{cm}^3 \text{K mol}^{-1}$ at 8 K and then decreases on further cooling. For complex **2**, the $\chi_M T$ value almost is constant above 80 K and then gradually decreases to 14.02 $\text{cm}^3 \text{K mol}^{-1}$ at 20 K, below which the $\chi_M T$ value increases to a maximum of 14.23 $\text{cm}^3 \text{K mol}^{-1}$ at 9 K and then rapidly decreases to 12.89 $\text{cm}^3 \text{K mol}^{-1}$ at 2 K. For both complexes, the decrease of $\chi_M T$ upon lowering of the temperature in the high-temperature range is most probably governed by depopulation of the Ln^{III} Stark sublevels. The increase of $\chi_M T$ at low temperature suggests the presence of ferromagnetic interactions between the Ln^{III} ions and the coordinated NO group of organic radicals, which may be due to a spin polarization mechanism of the unpaired electron of the radical ligand on the Ln^{III} empty orbitals. The observed ferromagnetic interaction is in agreement with those reported for similar Ln^{III} radical complexes in the literature.^{10,11}

The field dependences of magnetization (M) for the two complexes have been determined at 2 K in the range of 0–50 kOe (Figures S4 and S6 in the SI). Upon an increase in the applied field, M increases up to 6.7 and 7.1 $\text{N}\beta$ at 50 kOe for **1** and **2**, respectively, but does not reach the expected saturation values of 10 and 11 $\text{N}\beta$ (9 $\text{N}\beta$ for each Tb^{III} ion for $J = 6$ and $g = 3/2$ and 10 $\text{N}\beta$ for each Dy^{III} ion for $J = 15/2$ and $g = 4/3$, respectively, plus 1 $\text{N}\beta$ for each organic radical), indicating the presence of a magnetic anisotropy and/or low-lying excited states in the system, which corresponds to the reported results.^{8c,12} In addition, the M versus H plots for **1** and **2** do not show hysteresis above 2.0 K (Figures S5 and S7 in the SI).

To examine the spin dynamics, the ac measurements were carried out under a zero direct-current (dc) field with an ac field of 3 Oe with oscillating frequencies. Complex **1** shows frequency-dependent in-phase (χ') and out-of-phase (χ'') signals (Figure 3), indicating the presence of slow magnetic

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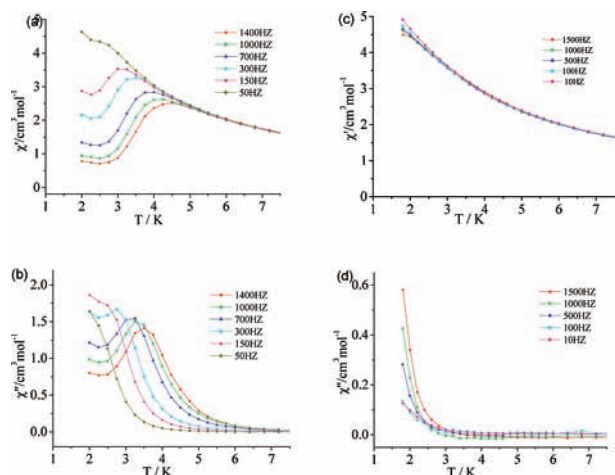


Figure 3. Temperature dependence of the in-phase (part a for **1** and part c for **2**) and out-of-phase (part b for **1** and part d for **2**) components of the ac magnetic susceptibility in 0 (for **1**) and 1 kOe (for **2**) dc fields with an oscillation of 3 Oe.

relaxation at low temperature, which is a diagnosis of a SMM.

The shift of the peak temperature (T_p) of in-phase signal (χ') is measured by a parameter $\varphi = (\Delta T_p/T_p)/\Delta(\log f) = 0.44$, which excludes the possibility of a spin glass ($0.01 < \varphi < 0.08$).¹³ Analysis of the frequency dependence of the χ'' peaks through Arrhenius law [$\tau = \tau_0 \exp(\Delta/k_B T)$], where T is the temperature of the maximum χ'' at different frequencies and $\tau = 1/2\pi\nu$] permits the estimation of magnetization relaxation parameters: the preexponential factor $\tau_0 = 9.56 \times 10^{-7}$ s and the energy barrier for the relaxation of the magnetization $\Delta/k_B = 17.1$ K with $R = 0.9997$ (Figure 4) in accordance with the behavior of SMMs.¹⁴ The obtained values of τ_0 and Δ are comparable to those of reported Tb-based SMMs.^{5a,b,15} On the basis of the crystal structure, the Tb^{III} ion lies in an unsymmetrical coordination geometry deriving from the nitronyl nitroxide radicals and hfac, which will afford an easy-axis anisotropy.^{10b,d} This ligand field can lift the 13-fold degeneracy of the $J = 6$ ground multiplet state of the Tb^{III} ion and yield a situation where the lowest substates formally corresponding to $J_z = \pm 6$ are considerably separated from

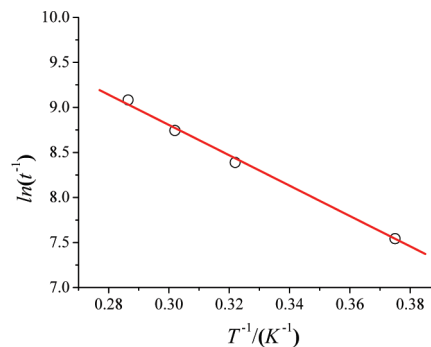


Figure 4. Plot of $\ln(\tau^{-1})$ versus T^{-1} fitting to the Arrhenius law for complex **1**.

the rest of the substates and lead to a higher thermal barrier between $J_z = +6$ and -6 .¹⁶ In addition, the ferromagnetic interactions between Tb^{III} and the radical could enhance the anisotropy.^{5d} Thus, slow magnetic relaxation behavior may be observed in **1**. For complex **2**, under the same conditions, no frequency-dependent signals were observed above 2 K, as shown in Figure S8 (see the SI), owing to the fast quantum-tunneling relaxation process.^{10a} As is well-known, the tunneling mechanism can be suppressed by applying a static magnetic field. So we recorded ac susceptibility versus temperature in a 1 kOe dc field. As a result, out-of-phase signals are visible and frequency-dependent (Figure 3), indicating likely SMM behavior.

In conclusion, we use a chelating pyridine-substituted nitronyl nitroxide radical ligand to obtain two radical lanthanide complexes. As far as we are aware, they are the first reported mononuclear rare-earth–radical systems with a chelating nitronyl nitroxide radical to exhibit slow magnetic relaxation. This work provides a new chemical route to obtain lanthanide radical SMMs.

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Supporting Information Available: Crystallographic files in CIF format and additional synthetic, structural, and magnetical data for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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