A family of lanthanide compounds based on nitronyl nitroxide radicals: synthesis, structure, magnetic and fluorescence properties†

Xue-Hui Lv,a Shuai-Liang Yang,a Yuan-Xia Li,a Chen-Xi Zhang ab and Qing-Lun Wang b,c

A series of lanthanide nitronyl nitroxide radical compounds, [Ln(hfac)3(NITPh-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide)exterch2](Ln = La (1), Eu (2), Gd (3), Tb (4), Dy (5), Er (6), hfac = hexafluoroacetylacetonate; NITPh-p-N(CH3)2-xC7H16 (Ln = La (1), Eu (2), Gd (3), Tb (4), Dy (5), Er (6)) have been synthesized and structurally characterized. X-Ray crystallographic analyses show that the structures of the six compounds are similar and all consist of isolated molecules, in which central Ln(III) ions are coordinated to six oxygen atoms from three hexafluoroacetylacetonate ligands and two oxygen atoms from nitronyl nitroxide radicals. Variable-temperature magnetic susceptibility studies reveal ferromagnetic interactions between the Gd(III) ion and nitronyl nitroxide radical in complex 3. Ac magnetic susceptibility measurements of complexes 4 and 5 exhibit frequency-dependent out-of-phase signals, indicating single-molecule magnet (SMM) behavior.

The stability of the radicals like nitronyl nitroxide at a relatively high temperature has made them potential systems in molecular magnetism.3 Recently, nitronyl nitroxides and lanthanide ions were successfully synthesized to obtain the SMMs and SCMs,4 especially heavy lanthanide ions such as terbium(III) and dysprosium(III). Since the terbium(III) and dysprosium(III) ions have large anisotropies,5 synthesis and characterization of terbium(III) and dysprosium(III) with the nitronyl nitroxide have already set the fashion in the field of molecular magnetism.5–11 For example, complex [Tb3(hfac)4(NIT-2thienyl)3]6 showed the coexistence of spin canting, metamagnetism, spin dynamic relaxation and magnetic ordering.11 [Dy(hfac)3(PyNO)]2 shows a remarkable SMM behavior with complex hysteresis at 1.4 K.12 One-dimensional chain complex [Tb(hfac)3(NITPhSCH3)2]10 is the first example of radical–metal SMM units in the construction of an SCM system.13

It is very interesting to develop new nitronyl nitroxide complexes and better understand the nature of 2p–4f magnetic interaction. In this paper, by using a new nitronyl nitroxide radical NITPh-p-N(CH3)2 and lanthanide ions, a series of novel 2p–4f complexes were synthesized. Herein we report a detailed study of the magnetic properties of a novel family of 2p–4f complexes: [Ln(hfac)3(NITPh-p-N(CH3)2)xC7H16]y (Ln = La (1), Eu (2), Gd (3), Tb (4), Dy (5) and Er (6), x = 2/3 for complexes 1, 2, 3 and 6 while 0 for 4 and 5). Complexes 4 and 5 present slow relaxation of the magnetization at low temperature, suggesting single-molecule magnet behavior.

Introduction

The study of molecular nanomagnets showing slow relaxation of the magnetization is one of the key topics in the field of molecular magnetism.1 Molecular nanomagnets mainly include single-molecule magnets (SMMs)2 and single-chain magnets (SCMs).3 SMMs and SCMs not only permit the observation of fascinating quantum phenomena but also are investigated as potential candidates for future high-density data storage materials. SMMs and SCMs exhibit slow relaxation of magnetization due to a large ground-state spin quantum number (S), a significant uniaxial magneto-anisotropy (D < 0), and a good magnetic isolation of the molecule.

Lanthanide (Ln) ions have become attractive candidates for constructing new SMMs and SCMs because most of them have significant magnetic anisotropy arising from the large unquenched orbital angular momentum. As a result, many lanthanide complexes with SMM behavior have become attractive synthetic targets for chemists.4

†Electronic supplementary information (ESI) available: Appendix A. CCDC 1063970 (1), 1063969 (2), 1063967 (3), 1063968 (4), 957789 (5), 1063966 (6) contain the supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ra05764d

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Experimental section

Materials and physical measurements

All reagents and solvents were purchased from commercial sources and used without purification. Ln[hfac]3·2H2O (La, Eu, Gd, Tb, Dy, Er)12 and NITPh-p-N(CH3)2 (ref. 13) were synthesized according to the reported methods.

Infrared spectra were recorded on a Perkin Elmer Spectrum One spectrometer using KBr pellets in the region 4000–400 cm⁻¹. Elemental analyses for C, H, and N were measured by a Perkin-Elmer 240 elemental analyzer. The X-ray powder diffraction patterns (PXRD) have been recorded on a Shimadzu LabX XRD-6100 diffractometer, operated at 40.0 kV and 30.0 mA, using a Cu target tube and graphite monochromator. The intensity data were recorded by continuous scan in 2θ/θ mode from 5° to 50° with a step size of 0.02° and a scan speed of 3° min⁻¹. The thermogravimetry-differential thermal analysis (TG-DTA) was studied by SDT-Q600 at a heating rate of 20 °C min⁻¹ in nitrogen atmosphere, and nitrogen gas of high purity (>99.999%) was used as carrier gas. The sample was heated from ambient temperature to 600 °C. Luminescence properties were recorded on an F-4500 FL spectrophotometer with a xenon arc lamp as the light source. The magnetic measurements were carried out with a MPMS XL-7 SQUID magnetometer. The samples were embedded in grease to avoid preferential orientation of the micro-crystallites. Diamagnetic corrections were made with Pascal’s constants for all of the constituent atoms.14

Synthesis procedures

Syntheses of [La(hfac)3(NITPh-p-N(CH3)2)2]·2/3C7H16 (1). 41 mg (0.05 mmol) of La(hfac)3·2H2O was dissolved in 15 mL of boiling heptanes for azeotropically removing hydration water of molecules. Then the solution was cooled to 70 °C, a solution of NITPh-p-N(CH3)2 (30 mg, 0.1 mmol) in 3 mL CH2Cl2 was added. The resulting blue solution was stirred for 15 min and cooled down to room temperature. The filtrate was allowed standing for 5 days, and dark green crystals suitable for X-ray diffraction were obtained. Anal. calc. for C45H70F18LaN6O10 (yield: 43%): C 39.74%, H 5.15%, N 6.14%. IR (KBr) ν/cm⁻¹: 1610 (vs), 1558 (w) 1531 (w), 1379 (w), 1346 (w), 1256 (vs), 1204 (vs), 1103 (w), 739 (w), 626 (w).

Syntheses of [Eu(hfac)3(NITPh-p-N(CH3)2)2]·2/3C7H16 (2). Compound 2 was obtained in a similar manner for 1 except that Eu(hfac)3·2H2O was used instead of La(hfac)3·2H2O. Anal. calc. for C45H70F18EuN6O10 (yield: 42%): C 40.44%, H 5.24%, N 6.29%. Found: C 40.23%, H 5.18%, N 6.19%. IR (KBr) ν/cm⁻¹: 1650 (vs), 1606 (w) 1552 (w), 1378 (w), 1359 (w), 1256 (vs), 1200 (vs), 1098 (w), 734 (w), 665 (w).

Syntheses of [Gd(hfac)3(NITPh-p-N(CH3)2)2]·2/3H2O (3). Compound 3 was obtained in a similar manner for 1 except that Gd(hfac)3·2H2O was used instead of La(hfac)3·2H2O. Anal. calc. for C45H70F18GdN6O10 (yield: 43%): C 39.89%, H 5.17%, N 6.20%. Found: C 39.96%, H 5.20%, N 6.25%. IR (KBr) ν/cm⁻¹: 1609 (vs), 1556 (w), 1375 (w), 1347 (w), 1255 (vs), 1198 (vs), 1095 (w), 791 (w), 664 (w).
Table 1  Crystal data and structure refinements for complexes 1–6

| Compound | Formula | Fw | Crystal system | Space group | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) | V (Å³) | Z | Dcalcd (Mg m⁻³) | μ (mm⁻¹) | F(0 0 0) | Crystal size (mm³) | θ range for data collection (°) | Reflections collected/unique | Rint | Data/restraints/parameters | GOF on F² | R1 [I > 2σ(I)] | wR1 (all data) | wR2 (all data) |
|----------|---------|----|----------------|-------------|------|------|------|------|------|------|-------|------|-----------------|----------|----------|-----------------|----------------|----------------|--------|------------------|-------------|--------------|-------------|-------------|
| 1 | C₁₄₉H₁₁₂₄La₃F₅₄N₁₈O₃₀ | 4138.78 | Monoclinic | C2/c | 50.575(6) | 12.6932(12) | 28.871(3) | 90 | 90 | 90 | 18 298(3) | 4 | 1.511 | 0.816 | 8360 | 0.24×0.22×0.22 | 1.84–25.02 | 68 912/15 954 | 0.0786 | 15 954/295/1244 | 1.143 | 0.0468 | 0.0508 | 0.1180 |
| 2 | C₁₄₉H₁₁₂₄Eu₃F₅₄N₁₈O₃₀ | 4177.93 | Monoclinic | C2/c | 50.142(5) | 12.6433(12) | 28.692(2) | 90 | 90 | 90 | 17 389(3) | 4 | 1.566 | 1.169 | 8432 | 0.24×0.22×0.22 | 1.45–25.02 | 68 008/15 737 | 0.0381 | 15 737/295/1244 | 1.118 | 0.0388 | 0.0407 | 0.0898 |
| 3 | C₁₄₉H₁₁₂₄Gd₃F₅₄N₁₈O₃₀ | 4193.80 | Monoclinic | C2/c | 49.926(3) | 12.6037(5) | 28.6406(16) | 90 | 90 | 90 | 17 674(16) | 4 | 1.576 | 1.241 | 8444 | 0.24×0.22×0.22 | 1.45–25.02 | 70 381/15 574 | 0.0423 | 15 574/295/1244 | 1.059 | 0.0320 | 0.0346 | 0.0800 |
| 4 | C₁₄₉H₁₁₂₄Tb₃F₅₄N₁₈O₃₀ | 3998.42 | Monoclinic | C2/c | 49.914(19) | 12.461(4) | 28.558(10) | 90 | 90 | 90 | 17 386(11) | 4 | 1.528 | 1.333 | 7992 | 0.22×0.22×0.22 | 1.46–25.02 | 59 484/15 238 | 0.0540 | 15 238/228/1183 | 1.045 | 0.0433 | 0.0511 | 0.1164 |
| 5 | C₁₄₉H₁₁₂₄Dy₃F₅₄N₁₈O₃₀ | 1336.39 | Monoclinic | C2/c | 12.6610(12) | 17.3720(15) | 24.491(2) | 90 | 90 | 90 | 5373.8(8) | 4 | 1.652 | 8.547 | 2668 | 0.20×0.20×0.20 | 1.46–25.02 | 43 328/10 500 | 0.0807 | 10 500/57/762 | 1.080 | 0.0587 | 0.0685 | 0.1682 |
| 6 | C₁₄₉H₁₁₂₄Er₃F₅₄N₁₈O₃₀ | 4223.83 | Monoclinic | C2/c | 12.6610(12) | 17.3720(15) | 24.491(2) | 90 | 90 | 90 | 17 733(7) | 4 | 1.582 | 1.535 | 8492 | 1.81×0.18×0.18 | 1.45–25.02 | 68 448/15 647 | 0.0360 | 15 647/474/1370 | 1.072 | 0.0504 | 0.0524 | 0.1182 |

Fig. 1. In complex 3, the Gd(m) ion is eight-coordinated in slightly distorted dodecahedron geometry. Two oxygen atoms of the N–O groups from nitronyl nitroxide radicals and six oxygen atoms from three different hfac anions are coordinated to the metal ions. The bond lengths of Gd(1)–O(radical) are Gd(1)–O(1) 2.3328(20) Å and Gd(1)–O(3) 2.3481(22)–2.4155(20) Å. These bond lengths are comparable to the reported lanthanide–nitronyl nitroxide complexes. The angles between the N–O groups from two radical ligands and Gd(m) ion are: N(1)–O(1)–Gd(1) 137.429(16)°, N(4)–O(3)–Gd(1) 138.962(16)° and O(1)–Gd(1)–O(3) 139.416(68)°. The nitronyl nitroxide moiety O1–N1–C1–N2–O2 makes a dihedral angle of 2.020(24)° with the plane of benzene ring.

In complex 3, the intermolecular hydrogen bonds occur between one carbon atom from one radical group and one fluorine atom from another hfac ion group (3.364 Å, C(6)–H(6A)···F(16)). This kind of alternate hydrogen bonds form 1D chain structure in complex 3, which is demonstrated in Fig. 2.

The structure of the complexes 1, 2, 4, 5 and 6 are similar to complex 3, except for the substitution of Gd(m) with La(m), Eu(m), Tb(m), Dy(m) and Er(m) ions, which makes the bond distances and angles vary a little (Table S1†). In complex 1, the nitronyl nitroxide moiety O1–N1–C1–N2–O2 makes a dihedral angle of 1.556(27)° with the plane of benzene ring, while in complex 2 is 1.861(35)°, complex 4 is 2.493(37)°, complex 5 is 4.061(43)° and complex 6 is 3.212(57)°. The structure of complexes 1, 2, 4, 5 and 6 is shown in Fig. S1–S5 (ESI†).

The shape measure
There are many kinds of coordination geometries in eight-coordinated complexes. Three high-symmetry polyhedra are used as a method of analysis of the shape. They are: the trigonal bipyramid (TBP), the bicapped trigonal prism (C₂ᵥ-TP), and the square antiprism (D₄ᵥ-AP) respectively. There exists an intrinsic relationship between the dihedral angles (one for each

Fig. 1  The crystal structure of complex 3. Fluorine and hydrogen atoms are not shown for the sake of clarity.
pair of adjacent triangular planes) and the notion of shape, i.e., the symmetry. Therefore, the geometry of complexes was analyzed by comparing all observed dihedral angles in a given structure and the corresponding ideal values.

Based on the crystal data, we carried out the calculations of the shape factor \( S \) to estimate the degree of distortion of the coordination structure in first coordination sphere. The \( S \) value is the minimal variance of dihedral angles along all edges given by eqn (1):

\[
S(\delta, \theta) = \text{min} \left( \frac{1}{m} \sum_{i=1}^{m} (\delta_i - \theta)^2 \right),
\]

in which \( m \) is the number of possible edges (\( m = 18 \) in this study), \( \delta_i \) and \( \theta \) are the dihedral angle between planes along the \( i \)th edge, in particular, the value of \( \delta_i \) is measured in a given structure and the value of \( \theta \) is observed in an ideal structure respectively. The observed dihedral angle between planes along the \( i \)th edge (\( \delta_i \)), the dihedral angle for the ideal structure (\( \delta_i \)) and the estimated \( S \) values of complexes 1–6 are listed in Tables S2–S7 (ESI†).

The following \( S \) values of shape measures calculations are showed in Table 2. By comparing the value of \( S \), the coordination environments of complexes 1–6 are all distorted dodecahedron.

### Powder X-ray diffraction and TG analyses

To confirm whether the crystal structures are truly representative of the bulk materials, the X-ray powder diffraction patterns (PXRD) of complexes 1–6 have been recorded which are shown in Fig. S6–S8 (ESI†). These patterns indicate that the PXRD patterns are in good agreement with the results simulated from the single crystal date, indicating the purity of the bulk-synthesized materials.

In order to investigate the thermal stability of complexes 1–6, the thermogravimetry-differential thermal analysis (TG-DTA) was studied, and the TG-DTA curve is depicted in Fig. S9–S11 (ESI†). The TG-DTA curves of 1–6 were similar. Herein, complex 1 as a representative example is selected to describe the thermal stability in details. For complex 1, the first stage takes place from 25.00 to 150 °C (the peak of DTA at 150.83 °C) with the weight loss of 11%, corresponding to losing solvent molecules. The second stage takes place from 150 to 500 °C (the peak of DTA at 302.35 °C) with the weight loss of 70%, corresponding to the skeleton of compound begins collapsed, implying the decomposition of hfac and (NITPh-p-N(CH₃)₂).

### Luminescence properties

The luminescent measurements of complexes 2 and 4 were investigated at room temperature in ethanol solution. The results reveal that these compounds exhibit the characteristic emission peaks. For complex 2 (Fig. 3, top), the excitation wavelength for emission spectra is 325 nm. The emission spectra are composed of four main bands at 591 nm \((^7D_0 \rightarrow ^7F_1)\), 614 nm \((^7D_0 \rightarrow ^7F_2)\), 650 nm \((^7D_0 \rightarrow ^7F_3)\), and 700 nm \((^7D_0 \rightarrow ^7F_4)\). The electric dipole transitions emission peak at 614 nm \((^7D_0 \rightarrow ^7F_2)\) is clearly stronger than the magnetic dipole transitions peak at 591 nm \((^7D_0 \rightarrow ^7F_1)\). The fluorescence spectra show the characteristic emission peaks of europium ions. For complex 4 (Fig. 3, bottom), the excitation wavelength for emission spectra is 325 nm. The emission spectra are composed of four main bands at 591 nm \((^7D_0 \rightarrow ^7F_1)\), 614 nm \((^7D_0 \rightarrow ^7F_2)\), 650 nm \((^7D_0 \rightarrow ^7F_3)\), and 700 nm \((^7D_0 \rightarrow ^7F_4)\). The electric dipole transitions emission peak at 614 nm \((^7D_0 \rightarrow ^7F_2)\) is clearly stronger than the magnetic dipole transitions peak at 591 nm \((^7D_0 \rightarrow ^7F_1)\). The fluorescence spectra show the characteristic emission peaks of europium ions.
wavelength for emission spectra is 290 nm. The emission peak at 490 nm could be attributed to the $^{5}D_{4} \rightarrow ^{7}F_{6}$ transition, and the other three peaks at 544, 582, and 619 nm could be assigned to the $^{5}D_{4} \rightarrow ^{7}F_{5}$, $^{5}D_{4} \rightarrow ^{7}F_{4}$, and $^{5}D_{4} \rightarrow ^{7}F_{3}$ transitions, respectively. Among them, the $^{5}D_{4} \rightarrow ^{7}F_{3}$ transition is the strongest. The fluorescence spectra show the characteristic emission peaks of terbium ions.

**Magnetic properties**

**Static magnetic properties of 1–6.** The temperature dependence of the magnetic susceptibilities of complexes 1–6 were measured for polycrystalline sample in the temperature range 2–300 K under an external magnetic field of 1 kOe. The magnetic behaviors for complexes 1–6 are shown in Fig. 4 and 5.

The room temperature values of $\chi_{M}T$ are 0.73, 8.64, 14.81, 14.80, and 12.69 cm$^3$ mol$^{-1}$ K for 1, 2, 3, 4, 5, 6 respectively, in good agreement with the expected values of 0.75, 8.63, 14.92, and 12.23 cm$^3$ mol$^{-1}$ K for one free Ln$^{III}$ ion (La$^{III}$, Eu$^{III}$, Gd$^{III}$, Tb$^{III}$, Dy$^{III}$, Er$^{III}$, Tm$^{III}$, Ho$^{III}$, and Pr$^{III}$) plus two isolated radicals ($g = 2, S = 1/2; 7F_{3}$, $S = 1/2; 7F_{4}$). As $T$ decreases to room temperature, the magnetic susceptibility value continuously decreases to reach a minimum of 0.38 cm$^3$ mol$^{-1}$ K for 1, 0.419 cm$^3$ mol$^{-1}$ K for 2, 5.89 cm$^3$ mol$^{-1}$ K for 4, 10.41 cm$^3$ mol$^{-1}$ K for 5 and 11.89 cm$^3$ mol$^{-1}$ K for 6 at $T = 2$ K. This probably governed by the depopulation of the Stark sublevels and/or significant antiferromagnetic interaction.

For complex 1, since the La$^{III}$ ion is diamagnetic, the magnetic analysis was thus carried out by using the isotropic spin Hamiltonian $H = -2J(\mathbf{S}_{1} \cdot \mathbf{S}_{2})$ (eqn (2)). Also, intermolecular exchange interaction ($zJ'$) in the molecular field approximation was involved (eqn (3)).

$$\chi'_{M} = \frac{2Ng^{2}\beta^{2}}{KT} \left[ \frac{1}{3 + \exp(-2J/KT)} \right]$$  \hspace{1cm} (2)

$$\chi_{M} = \frac{\chi'_{M}}{1 - (zJ'/Ng^{2}\beta^{2})\chi'_{M}}$$  \hspace{1cm} (3)

in which $J$ is intramolecular exchange integral between radicals, and $zJ'$ is the intermolecular interaction. The points below 45 K cannot be reproduced well with this model. The best fitting above 45 K gives $g = 2.01, J = -8.2$ cm$^{-1}$ and $zJ' = 1.1$ cm$^{-1}$. The negative value of $J$ indicates the antiferromagnetic interaction between nitronyl nitroxide radicals. Moreover, the little positive of $zJ'$ shows the very weak ferromagnetic interaction between two adjacent molecules. The plot of $\chi_{M}^{-1}$ vs. $T$ obeys the Curie-Weiss law.
Weiss law between 300 and 2 K, and yields $C = 0.756 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ with $\theta = -12.8 \text{ K}$. The negative value of $\theta$ further confirms the existence of antiferromagnetic coupling between spin carriers.

For complex 3, with the temperature decreases, the $\chi_M T$ value gradually increases to a maximum of 10.03 cm$^3$ mol$^{-1}$ K at 7.97 K, indicating the existence of ferromagnetic coupling between Gd(III) ion and nitronyl nitroxide. Below 7.97 K, $\chi_M T$ decreases quickly to 9.84 cm$^3$ mol$^{-1}$ K at 1.99 K. Based on the isotropic Hamiltonian $H = -J_1 \hat{S}_{\text{Gd}} \cdot S_{\text{rad}} + S_{\text{rad}} \cdot S_{\text{rad}}$, where $J_1$ and $J_2$ represent the magnetic coupling for the Gd–radical and radical–radical, respectively.

$$\chi_M = \frac{Ng^2\beta^2}{6kT} \left[ \frac{105 + 479 \exp \left( \frac{16J_1}{kT} \right) + 252 \exp \left( \frac{7J_1}{kT} \right) + 252 \exp \left( \frac{9J_1 - 2J_2}{kT} \right)}{6 + 10 \exp \left( \frac{16J_1}{kT} \right) + 8 \exp \left( \frac{7J_1}{kT} \right) + 8 \exp \left( \frac{9J_1 - 2J_2}{kT} \right)} \right]$$

The best fitting results give $J_1 = 2.0 \text{ cm}^{-1}, J_2 = -7.8 \text{ cm}^{-1}$ and $g = 2.00$, which is in the range for other similar Gd–radical compounds.\(^4\) The positive value of $J_1$ shows the ferromagnetic coupling between the Gd(III) ion and nitronyl nitroxide radical, while the negative $J_2$ indicates the next nearest-neighbor (NNN) antiferromagnetic coupling between the intramolecular radicals. The plot of $\chi_M^{-1}$ vs. $T$ obeys the Curie–Weiss law $1/\chi_M = (T - \theta)/C$ between 300 and 2 K, and yields $C = 8.8 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ with $\theta = 3.2 \text{ K}$. The positive value of $\theta$ further confirms the existence of ferromagnetic coupling between spin carriers. The magnetization data of the field dependent magnetization at 2.0 K (Fig. S12†) climbs up quickly until 10 kOe, and then rises up gradually to 70 kOe with an effective moment of 8.38 $\mu_B$, which is in smaller than the expected value of $S = 9/2$ under ferromagnetic interaction per GdRad$_2$ unit (9.00 $\mu_B$), indicating significant spin frustration behaviour because of the competing exchange interactions between $J_1$ and $J_2$.

**Dynamic magnetic properties of 4 and 5.** To study the slow relaxation of the magnetization of compounds 4 and 5, ac magnetic susceptibility studies were performed in a zero applied dc field, which were oscillating at frequencies in the range 111–2311 Hz. For complexes 4 and 5, no peaks of frequency-dependent in-phase signals ($\chi'$) were observed (Fig. 6 for 5 and Fig. S13 for 4 in the ESI†), moreover, the out-of-phase susceptibilities ($\chi''$) clearly display frequency-dependent signals, which indicate the presence of slow magnetic relaxation in complexes 4 and 5.\(^23\) No peaks of frequency-dependent out-phase signals ($\chi''$) were observed, which revealed that the quantum tunneling mechanical (QTM) process in 4 and 5 are pronounced. In order to reduce the QTM effect, the variable-temperature ac susceptibilities were determined again under a dc field of 2000 Oe (Fig. 7 for 5 and Fig. S14 for 4 in the ESI†). For 5, good peak shapes in both in-phase ($\chi'$) and out-of-phase ($\chi''$) curve were evidently observed; these phenomena indicate that the QTM effect is basically suppressed in 5 under an external 2000 Oe dc field. However, there are still no maxima peaks in both in-phase and out-of-phase curve for complex 4, which illustrate larger QTM effect in 4.

For complex 5, the Cole–Cole diagrams (Fig. 8), which were measured at temperatures of 2.0, 2.2 and 2.4 K, exhibit a quasi-semicircular shape that can be fitted to the generalized Debye model with $\alpha$ values of 0.34, 0.39 and 0.37, from 2 K to 2.4 K. The parameter $\phi$ ($\phi = (\Delta T_T/\Delta \log f)$) was calculated and a value of 0.36 was obtained, which excludes the possibility of a spin-glass ($0.01 < \phi < 0.08$).\(^{21}\) Plots of $\ln \tau$ versus $T^{-1}$ display linear dependence indicating spin reversal by the thermally activated Orbach mechanism process (Fig. 9). The Arrhenius fit ($\tau = \tau_0 \exp(\Delta_{\text{eff}}/k_B T)$) gives the effective energy barrier ($\Delta_{\text{eff}}/k_B$) of (23.44 ± 1.68) K and the pre-exponential $\tau_0$ of (7.15 ± 0.72) × 10$^{-9}$ s ($R = 0.925$) by $\chi'$ versus $T$ data under a dc field of 2000 Oe, which fall in the range well for SMMs.\(^{22,23}\)

![Fig. 7](Image) Frequency dependence of in-phase (top) and out-of-phase components of the ac magnetic susceptibility for 5 under 2000 Oe applied dc field.

![Fig. 8](Image) Cole–Cole plots of 5 under 2000 Oe. The black lines are results of fitting using the Debye model.
Conclusions

In summary, six lanthanide coordination complexes have been synthesized and structurally characterized. DC magnetic studies show that ferromagnetic metal–radical interactions take place in complex 3. AC magnetic studies for compounds 4 and 5 show clear frequency dependence of the out-of-phase susceptibility. With the application of external field (2000 Oe), good peak shapes of the out-of-phase and in-phase signals were obtained in 5, which give an energy barrier of $(23.44 \pm 1.68)$ K. It should be noted that multiple relaxation events can occur for single lanthanide sites. Thus, a more precise result must wait for low temperature measurements ($T < 1.0$ K) by using a micro-SQUID or more AC curves under different magnetic fields.

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