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

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

A series of lanthanide nitronyl nitrooxide radical compounds, [Ln(hfac)3(NITPh-N(CH3)2)xC7H16 (Ln = La (1), Eu (2), Gd (3), Tb (4), Dy (5), Er (6)], hfac = hexafluoroacetylacetonate; NITPh-N(CH3)2 = 4′-dimethylamino-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, x = 2/3 for complexes 1, 2, 3 and 6, and 0 for 4 and 5), 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 nitrooxide 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 nitrooxide 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,8 especially heavy lanthanide ions such as terbium(III) and dysprosium(III).7 Since the terbium(III) and dysprosium(III) ions have large anisotropies,8 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)9(NIT-2thien)3]n showed the coexistence of spin canting, metamagnetism, spin dynamic relaxation and magnetic ordering.9 [Dy(hfac)11(PyNO)]2 shows a remarkable SMM behavior with complex hysteresis at 1.4 K.10 One-dimensional chain complex [Tb(hfac)3(NITPhSCH3)]n is the first example of radical-metal SMM units in the construction of an SCM system.11

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-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-N(CH3)2)xC7H16] (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.
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) 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 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 5° 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%) with a flow rate of 100 mL min⁻¹ 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 are 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: 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), 1346 (w), 1256 (vs), 1198 (w), 1097 (w), 736 (w), 624 (w).

Syntheses of [Eu(hfac)3(NITPh-p-N(CH3)2)2]·2/3C7H16 (2). Compound 2 was obtained in a similar manner for complex 1 except that Eu(hfac)3·2H2O was used instead of La(hfac)3·2H2O. Anal. calc. for C45H70F18EuN6O10 (yield: 45%): C 40.05%, H 5.19%, N 6.23%. Found: C 39.94%, H 5.04%, N 6.14%. IR (KBr) ν/cm⁻¹: 1653 (vs), 1611 (w) 1553 (w), 1373 (w), 1347 (w), 1253 (vs), 1205 (vs), 1095 (w), 738 (w), 622 (w).

Syntheses of [Gd(hfac)3(NITPh-p-N(CH3)2)2]·2/3C7H16 (3). Compound 3 was obtained in a similar manner for complex 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).

Syntheses of [Tb(hfac)3(NITPh-p-N(CH3)2)2]·2H2O (4). Compound 4 was obtained in a similar manner for complex 1 except that Tb(hfac)3·2H2O was used instead of La(hfac)3·2H2O. Anal. calc. for C45H70F18TbN6O10 (yield: 40%): C 39.84%, H 5.16%, N 6.20%. Found: C 39.68%, H 5.02%, N 6.04%. IR (KBr) ν/cm⁻¹: 1609 (vs), 1609 (w) 1553 (w), 1375 (w), 1356 (w), 1254 (vs), 1198 (vs), 1097 (w), 736 (w), 624 (w).

Syntheses of [Dy(hfac)3(NITPh-p-N(CH3)2)2] (5). Compound 5 was obtained in a similar manner for complex 1 except that Dy(hfac)3·2H2O was used instead of La(hfac)3·2H2O. Anal. calc. for C45H70F18DyN6O10 (yield: 38%): C 39.74%, H 5.15%, N 6.18%. Found: C 39.66%, H 5.07%, N 6.03%. IR (KBr) ν/cm⁻¹: 1655 (vs), 1528 (w), 1387 (w), 1352 (w), 1255 (vs), 1199 (vs), 1095 (w), 795 (w), 661 (w).

Syntheses of [Er(hfac)3(NITPh-p-N(CH3)2)2]·2/3C7H16 (6). Compound 6 was obtained in a similar manner for complex 1 except that Er(hfac)3·2H2O was used instead of La(hfac)3·2H2O. Anal. calc. for C45H70F18ErN6O10 (yield: 36%): C 39.60%, H 5.13%, N 6.16%. Found: C 39.43%, H 5.01%, 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), 623 (w).

Crystal structure determination

Crystals of complexes 1–6 were mounted on glass fibers. Determination of the unit cell and data collection were performed with Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART 1000 diffractometer and equipped with a CCD camera. The ω–ϕ scan technique was employed. The structures were solved primarily by direct method and second by Fourier difference techniques and refined by the full-matrix least-squares method. The computations were performed with the SHELXL-97 program.15 Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. A summary of the crystallographic data and structure refinement is given in Table 1. Selected bond distances and angles for 1–6 are listed in Table S1 (see ESI†).

CCDC 1063970 (1), 1063969 (2), 1063967 (3), 1063968 (4), 957789 (5), 1063966 (6), contain the supplementary crystallographic data for this paper.†

Results and discussion

Crystal structure

Complexes 1, 2, 3, 4 and 6 crystallize in the monoclinic space group C2/c, while 5 crystallizes in the monoclinic space group P21/n. There are solvent molecules in complexes 1, 2, 3 and 6, while no solvent molecule in complexes 4 and 5. Crystal data and details of structural determination refinement are summarized in Table 1, and selected bond distances and angles for complexes 1–6 are listed in Table S1 in the ESI.†

The structural analyses show that complexes 1–6 are very similar; hence, only the crystal structure of complex 3 is described here. Complex 3 consists of the [Gd(hfac)3(NITPh-p-N(CH3)2)2] unit and solvent molecule of C7H16. The structure of [Gd(hfac)3(NITPh-p-N(CH3)2)2] unit in complex 3 is shown in
Table 1 Crystal data and structure refinements for complexes 1–6

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Space group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>V (Å³)</th>
<th>Z</th>
<th>Dcalcd (Mg m⁻³)</th>
<th>μ (mm⁻¹)</th>
<th>F(0 0 0)</th>
<th>Crystal size (mm³)</th>
<th>ρ range for data collection (°)</th>
<th>Reflections collected/unique</th>
<th>R(int)</th>
<th>Data/restraints/parameters</th>
<th>GOF on F²</th>
<th>R₁ [I &gt; 2σ(I)]</th>
<th>wR₁ [I &gt; 2σ(I)]</th>
<th>R₁ (all data)</th>
<th>wR₂ (all data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₁₄₉H₁₇₃La₃F₅₄N₁₈O₃₀</td>
<td>C2/c</td>
<td>50.575(6)</td>
<td>50.142(5)</td>
<td>28.871(3)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>18.298(3)</td>
<td>4</td>
<td>1.511</td>
<td>0.816</td>
<td>8360</td>
<td>0.26 × 0.24 × 0.26</td>
<td>1.84–25.02</td>
<td>68.912/15.954</td>
<td>0.0786</td>
<td>15 954/295/1244</td>
<td>1.143</td>
<td>0.0468</td>
<td>0.1155</td>
<td>0.0508</td>
<td>0.1180</td>
</tr>
<tr>
<td>2</td>
<td>C₁₄₉H₁₇₃Eu₃F₅₄N₁₈O₃₀</td>
<td>C2/c</td>
<td>50.575(6)</td>
<td>50.142(5)</td>
<td>28.871(3)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>18.298(3)</td>
<td>4</td>
<td>1.511</td>
<td>0.816</td>
<td>8360</td>
<td>0.26 × 0.24 × 0.26</td>
<td>1.84–25.02</td>
<td>68.912/15.954</td>
<td>0.0786</td>
<td>15 954/295/1244</td>
<td>1.143</td>
<td>0.0468</td>
<td>0.1155</td>
<td>0.0508</td>
<td>0.1180</td>
</tr>
<tr>
<td>3</td>
<td>C₁₄₉H₁₇₃Gd₃F₅₄N₁₈O₃₀</td>
<td>C2/c</td>
<td>50.575(6)</td>
<td>50.142(5)</td>
<td>28.871(3)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>18.298(3)</td>
<td>4</td>
<td>1.511</td>
<td>0.816</td>
<td>8360</td>
<td>0.26 × 0.24 × 0.26</td>
<td>1.84–25.02</td>
<td>68.912/15.954</td>
<td>0.0786</td>
<td>15 954/295/1244</td>
<td>1.143</td>
<td>0.0468</td>
<td>0.1155</td>
<td>0.0508</td>
<td>0.1180</td>
</tr>
<tr>
<td>4</td>
<td>C₁₄₉H₁₇₃Tb₃F₅₄N₁₈O₃₀</td>
<td>C2/c</td>
<td>50.575(6)</td>
<td>50.142(5)</td>
<td>28.871(3)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>18.298(3)</td>
<td>4</td>
<td>1.511</td>
<td>0.816</td>
<td>8360</td>
<td>0.26 × 0.24 × 0.26</td>
<td>1.84–25.02</td>
<td>68.912/15.954</td>
<td>0.0786</td>
<td>15 954/295/1244</td>
<td>1.143</td>
<td>0.0468</td>
<td>0.1155</td>
<td>0.0508</td>
<td>0.1180</td>
</tr>
<tr>
<td>5</td>
<td>C₁₄₉H₁₇₃DyF₅₄N₁₈O₃₀</td>
<td>C2/c</td>
<td>50.575(6)</td>
<td>50.142(5)</td>
<td>28.871(3)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>18.298(3)</td>
<td>4</td>
<td>1.511</td>
<td>0.816</td>
<td>8360</td>
<td>0.26 × 0.24 × 0.26</td>
<td>1.84–25.02</td>
<td>68.912/15.954</td>
<td>0.0786</td>
<td>15 954/295/1244</td>
<td>1.143</td>
<td>0.0468</td>
<td>0.1155</td>
<td>0.0508</td>
<td>0.1180</td>
</tr>
<tr>
<td>6</td>
<td>C₁₄₉H₁₇₃ErF₅₄N₁₈O₃₀</td>
<td>C2/c</td>
<td>50.575(6)</td>
<td>50.142(5)</td>
<td>28.871(3)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>18.298(3)</td>
<td>4</td>
<td>1.511</td>
<td>0.816</td>
<td>8360</td>
<td>0.26 × 0.24 × 0.26</td>
<td>1.84–25.02</td>
<td>68.912/15.954</td>
<td>0.0786</td>
<td>15 954/295/1244</td>
<td>1.143</td>
<td>0.0468</td>
<td>0.1155</td>
<td>0.0508</td>
<td>0.1180</td>
</tr>
</tbody>
</table>

The bond lengths of Gd(1)–Hfac are in the range of 2.3481(22)–2.3412(18) Å. The angles N(1)–O(1)–Gd(1) is 137.429(16)°, N(4)–O(3)–Gd(1) 138.956(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)–H6A···F(16)). This kind of alternate hydrogen bonds form 1D chain structure in complex 3, which is demonstrated in Fig. 2.

The crystal 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 prism (D₃d-DD), the bicapped trigonal prism (C₂ᵥ-TP), and the square antiprism (D₄d-AP) respectively. There exists an intrinsic relationship between the dihedral angles (one for each
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):

$$S(\delta, \theta) = \min_{m} \left[ \frac{1}{m} \sum_{j=1}^{m} (\delta_j - \theta_j)^2 \right],$$

in which $m$ is the number of possible edges ($m = 18$ in this study), $\delta_i$ and $\theta_i$ 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 $\theta_i$ 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 ($\theta_i$) 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.

**Table 2** $S$ values of shape-measure calculations for complexes 1–6

<table>
<thead>
<tr>
<th>Ln(III)</th>
<th>$S(D_{ad})$</th>
<th>$S(C_{ad})$</th>
<th>$S(D_{ad})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La (1)</td>
<td>6.08</td>
<td>12.06</td>
<td>9.73</td>
</tr>
<tr>
<td>Eu (2)</td>
<td>5.15</td>
<td>12.65</td>
<td>10.24</td>
</tr>
<tr>
<td>Gd (3)</td>
<td>4.95</td>
<td>12.62</td>
<td>10.43</td>
</tr>
<tr>
<td>Tb (4)</td>
<td>9.58</td>
<td>11.77</td>
<td>10.06</td>
</tr>
<tr>
<td>Dy (5)</td>
<td>5.51</td>
<td>20.98</td>
<td>18.52</td>
</tr>
<tr>
<td>Er (6)</td>
<td>4.83</td>
<td>20.53</td>
<td>10.58</td>
</tr>
</tbody>
</table>

**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 ($^{5}D_{0} \rightarrow ^{7}F_{1}$), 614 nm ($^{5}D_{0} \rightarrow ^{7}F_{2}$), 650 nm ($^{5}D_{0} \rightarrow ^{7}F_{3}$), and 700 nm ($^{5}D_{0} \rightarrow ^{7}F_{4}$). The electric dipole transitions emission peak at 614 nm ($^{5}D_{0} \rightarrow ^{7}F_{2}$) is clearly stronger than the magnetic dipole transitions peak at 591 nm ($^{5}D_{0} \rightarrow ^{7}F_{1}$). The fluorescence spectra show the characteristic emission peaks of europium ions.18 For complex 4 (Fig. 3, bottom), the excitation

**Figure 2** A sketch of the intermolecular hydrogen bonds of complex 3.

**Figure 3** Room-temperature luminescence spectra of complex 2 ($\lambda_{ex} = 325$ nm, top) and complex 4 ($\lambda_{ex} = 290$ nm, bottom) in ethanol solution.
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.\textsuperscript{19}

**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, 12.41, 14.80 and 12.69 cm$^3$ mol$^{-1}$ K for 1, 3, 4, 5, 6 respectively, in good agreement with the expected values of 0.75, 8.63, 12.23, 14.92 and 12.23 cm$^3$ mol$^{-1}$ K for one free Ln$^{III}$ ion (La$^{III}$, $^{5}D_{4}$; $^{5}D_{4}$; Dy$^{III}$; $^{5}D_{4}$; Gd$^{III}$, $^{5}D_{4}$; Tb$^{III}$, $^{5}D_{4}$; Er$^{III}$, $^{5}D_{4}$; Ho$^{III}$, $^{5}D_{4}$ plus two isolated radicals ($g = 2$, $S = 1/2$).\textsuperscript{19} For 2, the $\chi_M^T$ value at room temperature is 3.09 cm$^3$ mol$^{-1}$ K is much higher than the theoretical value of 0.75 cm$^3$ mol$^{-1}$ K for Eu$^{III}$ ion ($^{5}F_{J}$) in the ground state and two organic radicals ($S = 1/2$, $S = 3/2$, $S = 5/2$; $^{5}F_{J,5/2}$, $^{7}F_{5,5/2}$, $^{5}F_{J,3/2}$, $^{7}F_{5,3/2}$) plus two isolated radicals ($g = 2$, $S = 1/2$).\textsuperscript{19} For 4, the $\chi_M^T$ value at room temperature is 3.09 cm$^3$ mol$^{-1}$ K is much higher than the theoretical value of 0.75 cm$^3$ mol$^{-1}$ K for Eu$^{III}$ ion ($^{5}F_{J}$) in the ground state and two organic radicals ($S = 1/2$, $S = 3/2$, $S = 5/2$; $^{5}F_{J,5/2}$, $^{7}F_{5,5/2}$, $^{5}F_{J,3/2}$, $^{7}F_{5,3/2}$) plus two isolated radicals ($g = 2$, $S = 1/2$).\textsuperscript{19} For 5, the $\chi_M^T$ value at room temperature is 3.09 cm$^3$ mol$^{-1}$ K is much higher than the theoretical value of 0.75 cm$^3$ mol$^{-1}$ K for Eu$^{III}$ ion ($^{5}F_{J}$) in the ground state and two organic radicals ($S = 1/2$, $S = 3/2$, $S = 5/2$; $^{5}F_{J,5/2}$, $^{7}F_{5,5/2}$, $^{5}F_{J,3/2}$, $^{7}F_{5,3/2}$) plus two isolated radicals ($g = 2$, $S = 1/2$).\textsuperscript{19} For 6, the $\chi_M^T$ value at room temperature is 3.09 cm$^3$ mol$^{-1}$ K is much higher than the theoretical value of 0.75 cm$^3$ mol$^{-1}$ K for Eu$^{III}$ ion ($^{5}F_{J}$) in the ground state and two organic radicals ($S = 1/2$, $S = 3/2$, $S = 5/2$; $^{5}F_{J,5/2}$, $^{7}F_{5,5/2}$, $^{5}F_{J,3/2}$, $^{7}F_{5,3/2}$) plus two isolated radicals ($g = 2$, $S = 1/2$).\textsuperscript{19}

The temperature dependence of $\chi_M^T$ for complexes 2, 4, 5, 6 at 1000 Oe.

$$x'_M = \frac{2Ng^2\beta^2}{KT} \left[ \frac{1}{3 + \exp(-2J/KT)} \right]$$

$$x_M = \frac{\chi_M}{1 - (2zJ'/Ng^2\beta^2)x'_M}$$

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 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 \( H = -J_1 (\hat{S}_{\text{Gd}} \times \hat{S}_{\text{rad1}} + \hat{S}_{\text{Gd}} \times \hat{S}_{\text{rad2}}) - J_2 \hat{S}_{\text{rad1}} \times \hat{S}_{\text{rad2}} \), eqn (4) is introduced to analyse the magnetic coupling strength, where \( J_1 \) and \( J_2 \) represent the magnetic coupling for the Gd–radical and radical–radical, respectively.

\[
\chi_M = \frac{Ng^2 \beta^3}{6KT} \left( \frac{16J_1}{KT} \right) \exp \left( \frac{105 + 479 \exp \left( \frac{16J_1}{KT} \right) + 252 \exp \left( \frac{7J_1}{KT} \right) + 252 \exp \left( \frac{9J_1 - 2J_2}{KT} \right)}{6 + 10 \exp \left( \frac{16J_1}{KT} \right) + 8 \exp \left( \frac{7J_1}{KT} \right) + 8 \exp \left( \frac{9J_1 - 2J_2}{KT} \right)} \right)
\]

(4)

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.\(^{26}\) 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 \( \chi_M T \) 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.\(^{26}\) 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 \( \varphi \) (\( \varphi = (\Delta T_\psi T_\psi)/(\Delta \log f) \)) was calculated and a value of 0.36 was obtained, which excludes the possibility of a spin-glass (0.01 < \( \varphi < 0.08 \)).\(^{21}\) Plots of \( \ln \tau^{-1} \) versus \( T^{-1} \) display linear dependence indicating spin reversal by the thermally activated Orbach mechanism process (Fig. 9). The Arrenius 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 ac versus \( T \) data under a dc field of 2000 Oe, which fall in the range well for SMMs.\(^{22,23}\)
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.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21371104, 20771081, 21101096, and 21471084) and MOE Innovation Team (IRT13022) of China.

Notes and references


15 (a) G. M. Sheldrick, SHELXS 97, University of Göttingen, Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL 97, University of Göttingen, Göttingen, Germany, 1997.


