Three lanthanide–nitronyl nitroxide complexes: syntheses, crystal structures and magnetic properties

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ABSTRACT

One nitronyl nitroxide radical and its three mononuclear tri-spin compounds [Ln(hfac)₃(NIT-3py-6OCH₃)₂] (Ln = Gd **1**, Tb **2**, Dy **3** hfac = hexafluoroacetylacetonate; NIT-3py-6OCH₃ = 2-(3'-pyridine-6'-methoxyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide have been prepared and characterized. Single crystal X-ray analyses show that all these three complexes are isomorphous, which crystallize in *P*2₁/*n* space group and show similar radical-Ln(III)-radical structures. The center lanthanide(III) ions of them are eight-coordinate in distorted triangular dodecahedral LnO₈ coordination geometry completed by two NIT-3py-6OCH₃ radicals and three hfac[−] ligands. The magnetic studies reveal that ferromagnetic interactions (between intramolecular Ln and radical) and antiferromagnetic interactions (between the intramolecular radicals) are coexist in these complexes. Tb complex displays frequency-dependent signals at low temperature suggesting that it behaves as SMM.

1. Introduction

During the past two decades, much attention has been paid to the design and construction of single-molecule magnets (SMMs) [1–5]. This type of materials are characterized as slow magnetization relaxation caused by the association of large ground state spin (*S*_T) value with a significant uniaxial (Ising-like) magnetic anisotropy (*D*), which leads to a significant energy barrier to magnetization reversal (*U*) [6–9]. The SMMs have found potential applications in high-density information storage, quantum information processing, and spintronics at the molecular level [10–13]. It is well known that 4f metal ions are good candidates for the construction of SMMs due to their significant magnetic anisotropy arising from the large, unquenched orbital angular momentum. Up to now a variety of 4f metal ions based SMMs have been reported [14–18].

Among the different approaches to prepare molecular magnetic materials, the combination of different spin carriers within the same molecular entity is a widely employed strategy because (i) the orthogonality of the magnetic orbitals of two different spin carriers, which leads to a ferromagnetic interaction, can be reached much more easily than the accidental orthogonality within the homospin systems, and (ii) even if the magnetic coupling is antiferromagnetic, the resulting spin can be big enough when a large spin ($5/2$, $7/2$) interacts with a small one, such as a spin $1/2$ [3]. A variety of single-molecule magnets were prepared by this strategy [17,18]. Recently, the so called metal–radical strategy that combining paramagnetic organic molecules with metal ions give rise to complexes with different structure and magnetic properties have been received more and more attention since the discovery of the first radical–4f SMM by D. Gatteschi’s group [19]. The stable radical ligand can generate typically stronger intramolecular magnetic exchange coupling. The strong exchange-coupling between lanthanides and radicals generally leads to superior SMMs. In 2011, a binuclear Tb^{III} complex bridged by a $\text{N}_2^{\cdot-3-}$ radical has been reported with a record blocking temperature of 13.9 K [20,21]. For the past few years various organic radicals such as nitronyl nitroxide, verdazyl and semiquinone radicals have been reported [22–26]. However, researches so far are focused in particular on the nitronyl nitroxide (NIT) family of radicals, because this type of radicals are relatively stable and easy to obtain derivatives with substituents containing donor atoms.

In an effort to further study the magnetic properties of metal–radical complexes, we decided to employ 3-pyridine-6-methoxyl substituted nitronyl nitroxide as ligand to construct radical–4f compound. The nitrogen atom of pyridine and the oxygen atom of methoxyl group are good coordination atom. We hope that we can get novel structure complexes by this ligand. Finally we have successfully obtained three mononuclear tri-spin compounds. $[\text{Ln}(\text{hfac})_3(\text{NIT-3py-6OCH}_3)_2]$ [$\text{Ln} = \text{Gd}$ **1**, Tb **2**, Dy **3**; hfac = hexafluoroacetylacetonate; $\text{NIT-3py-6OCH}_3 = 2\text{-(3'-pyridine-6'-methoxyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide}$]. Complex **2** shows the presence of frequency-dependent signals at low temperature suggesting that it behaves as SMMs.

Scheme 1 Molecule structure of NIT-Ph-4-Br and hfac.

2. Experimental Section

2.1. Materials and physical measurements

All the starting chemicals were obtained from Aldrich and used without further purification. The radical ligand NIT-3py-6OCH₃ was prepared according to literature method [27]. Elemental analyses (C, H, N) were determined by Perkin–Elmer 240 elemental analyzer. The infrared spectra were recorded from KBr pellets in the range 4000–400 cm⁻¹ with a Bruker Tensor 27 IR spectrometer. The magnetic measurements were carried out with MPMSXL–7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

2.2. Synthesis of Gd(hfac)₃(NIT-3py-6OCH₃)₂ (**1**)

A solution of Gd(hfac)₃·2H₂O (0.0814 g 0.1 mmol) in 30 mL dry boiling heptane was heated to reflux for about 2 h. Then the solution was cooled to 60 °C, a solution of NIT-3Py-6OCH₃ (0.0529 g 0.2 mmol) in 4 mL of CH₂Cl₂ was added. The resulting solution was stirred for 5 min and then cooled it to room temperature. The filtrate was allowed to stand at room temperature for slow evaporation. After two days, the dark blue crystals were collected; yield 53 %. Anal. Calc. for C₄₁H₃₉F₁₈GdN₆O₁₂ (1307.03): calcd. C 37.67, H 3.01, N 6.43; found C 37.80, H 3.08, N 6.54. FT-IR (KBr): 3048 (w), 2397 (w), 1655 (s), 1512 (s), 1351 (s), 1202(s), 1144 (s), 798 (s), 662 (m), 586(m), 546(m) cm⁻¹.

2.3. Synthesis of Tb(hfac)₃(NIT-3py-6OCH₃)₂ (**2**)

Complex **2** was synthesized by the similar procedure as complex **1** but with Tb(hfac)₃·2H₂O instead of Gd(hfac)₃·2H₂O. Anal. Calc. for C₄₁H₃₉F₁₈TbN₆O₁₂ (1308.68): C, 37.63; H, 3.00; N, 6.42. Found: C, 37.48; H, 2.96; N, 6.29%. FT-IR (KBr, cm⁻¹): 3048 (w), 2398 (m), 1654(s), 1511(s), 1350 (s), 1201(s), 1145 (s), 798 (s), 662 (m), 586(m) 545(m) cm⁻¹.

2.4. Synthesis of Dy(hfac)₃(NIT-3py-6OCH₃)₂ (**3**)

Complex **3** was synthesized by the similar procedure as complex **1** but with Dy(hfac)₃·2H₂O instead of Gd(hfac)₃·2H₂O. Anal. Calc. for C₄₁H₃₉F₁₈DyN₆O₁₂ (1308.68): C, 37.53; H, 3.00; N, 6.40. Found: C, 37.69; H, 3.07; N, 6.57%. FT-IR (KBr, cm⁻¹): 3046 (w), 2397 (w), 1654(s), 1510(s), 1351(s), 1201(s), 1146(s), 799(s), 662(m), 586(m) 545(m) cm⁻¹.

2.5. X-ray crystal structure determinations

X-ray single-crystal diffraction data for complexes **1**, **2** and **3** were collected using a Rigaku Saturn CCD diffractometer at about 113 K with Mo K α radiation (λ = 0.71073 Å). The structure was solved by direct methods by using the program SHELXS-97 [28] and refined by full-matrix least-squares methods on F^2 with the use of the SHELXL-97 [28] program package. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal

parameter. Disordered carbon atoms were observed in the hfac ligands for both compounds. The pertinent crystallographic data and structure refinement parameters for complexes **1**, **2** and **3** were listed in Tables 1 and 2.

3. Results and discussion

3.1 Structural descriptions

Single crystal X-ray crystallographic analysis reveals that complexes **1**, **2** and **3** are isomorphous. Therefore, only the structure of complex **1** will be described in detail. As shown in Fig. 1, complex **1** is a tri-spin system with one Gd^{III} ions and two radicals, which crystallizes in the monoclinic space group $P2_1/n$. The central Gd^{III} ions are eight-coordinated in slightly distorted dodecahedron geometry. Six oxygen atoms from three hfacs with the Gd—O bond lengths in the range of 2.343(3) – 2.407(3) Å while two oxygen atoms from two radical molecules with the Gd(1)—O(3) bond length of 2.338(3) Å and Gd(1)—O(5) 2.361(3) Å. The nitronyl nitroxide radicals act as monodentate ligands to Gd^{III} ion through one N—O group, the N(2)—O(4) and N(3)—O(6) bond lengths are 1.286 Å, and 1.306 Å respectively while the uncoordinated N(1)—O(5) and N(4)—O(2) bond lengths are 1.259(5) Å and 1.271(5) Å respectively, which are comparable to those of reported tri-spin radical-Ln^{III}-radical complexes [29–41]. The two nitroxide ligands are trans and the angle of O(5)_{rad}–Gd–O(3)_{rad} is found to be 136.29(14)°. Packing arrangements of complex **1** are shown in Fig. 1. The nearest Gd··Gd distance is found to be 10.628(2) Å, the closest O··O (NO groups) distance is 2.823(2) Å which is much shorter than the corresponding intramolecular distance of 4.359(2) Å. The short contacts of radical spin centers indicate the nonnegligible dipolar–dipolar interactions in.

Fig. 1. Molecular structure of complex **1** (left) and packing diagram of complex **1** (right). All hydrogen atoms and fluorine atoms are omitted for clarity.

Table 1 Crystallographic data for complexes **1**, **2** and **3**.

	1	2	3
Formula	C ₄₁ H ₃₉ GdF ₁₈ N ₆ O ₁₂	C ₄₁ H ₃₉ TbF ₁₈ N ₆ O ₁₂	C ₄₁ H ₃₉ DyF ₁₈ N ₆ O ₁₂
Mr	1307.03	1308.70	1312.28
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$

<i>a</i> /Å	12.630(2)	12.602(3)	12.557(3)
<i>b</i> /Å	16.739(3)	16.705(4)	16.707(4)
<i>c</i> /Å	24.765(5)	24.799(6)	24.759(6)
<i>β</i> , deg	93.141(2)	93.398(4)	93.542(4)
<i>V</i> /Å ³	5227.6(16)	5211(2)	5184(2)
<i>Z</i>	4	4	4
<i>D_{calcd}</i> /g cm ⁻³	1.661	1.668	1.569
<i>T_{min}</i> and <i>T_{max}</i>	0.554 1.000	0.651 1.000	0.741 1.000
<i>θ_{min}</i> , <i>θ_{max}</i> deg	1.47, 25.01	1.51, 25.01	1.47, 25.01
<i>Reflections collected</i>	42953	41724	41256
<i>Unique reflns</i> / <i>R_{int}</i>	9150/ 0.0531	9099/ 0.0946	9094/ 0.0632
<i>GOF</i> (<i>F</i> ²)	0.978	0.964	1.035
<i>RI/wR2</i> (<i>I</i> > 2σ(<i>I</i>))	0.0425/0.1230	0.0525/ 0.1154	0.0390/ 0.1003
<i>RI/wR2</i> (<i>all data</i>)	0.0471/ 0.1272	0.0644/ 0.1243	0.0434/ 0.1036

Table 2 Selected important bond lengths (Å) and angles (°) for complexes **1**, **2** and **3**.

1		2		3	
Gd(1)-O(3)	2.336(2)	Tb(1)-O(3)	2.312(3)	Dy(1)-O(14)	2.299(3)
Gd(1)-O(8)	2.344(3)	Tb(1)-O(8)	2.318(3)	Dy(1)-O(5)	2.300(3)
Gd(1)-O(12)	2.362(3)	Tb(1)-O(9)	2.319(4)	Dy(1)-O(18)	2.314(3)
Gd(1)-O(5)	2.362(2)	Tb(1)-O(6)	2.338(3)	Dy(1)-O(26)	2.325(3)
Gd(1)-O(9)	2.389(3)	Tb(1)-O(11)	2.357(3)	Dy(1)-O(8)	2.349(3)
Gd(1)-O(10)	2.396(2)	Tb(1)-O(12)	2.361(3)	Dy(1)-O(6)	2.351(2)
Gd(1)-O(11)	2.401(3)	Tb(1)-O(7)	2.379(3)	Dy(1)-O(11)	2.363(3)
Gd(1)-O(7)	2.409(3)	Tb(1)-O(10)	2.379(3)	Dy(1)-O(1)	2.371(3)
O(3)-N(2)	1.312(4)	O(3)-N(5)	1.306(5)	O(5)-N(9)	1.310(4)
N(1)-O(2)	1.276(4)	O(6)-N(3)	1.295(5)	N(19)-O(23)	1.270(4)
O(5)-N(4)	1.293(4)	N(6)-O(2)	1.269(5)	O(33)-N(35)	1.273(4)
O(6)-N(5)	1.273(4)	N(2)-O(5)	1.277(5)	N(20)-O(26)	1.307(4)
O(3)-Gd(1)-O(8)	88.66(9)	O(3)-Tb(1)-O(8)	89.38(12)	O(14)-Dy(1)-O(5)	89.28(10)
O(3)-Gd(1)-O(12)	107.40(10)	O(3)-Tb(1)-O(9)	106.71(12)	O(14)-Dy(1)-O(18)	138.09(9)
O(8)-Gd(1)-O(12)	137.27(9)	O(8)-Tb(1)-O(9)	138.14(12)	O(5)-Dy(1)-O(18)	106.62(10)
O(3)-Gd(1)-O(5)	136.16(9)	O(3)-Tb(1)-O(6)	136.07(12)	O(14)-Dy(1)-O(26)	100.71(10)
O(8)-Gd(1)-O(5)	100.82(9)	O(8)-Tb(1)-O(6)	100.32(12)	O(5)-Dy(1)-O(26)	136.12(10)
O(12)-Gd(1)-O(5)	94.25(9)	O(9)-Tb(1)-O(6)	94.20(12)	O(18)-Dy(1)-O(26)	94.04(10)
O(3)-Gd(1)-O(9)	73.93(9)	O(3)-Tb(1)-O(11)	71.94(11)	O(14)-Dy(1)-O(8)	146.78(9)
O(8)-Gd(1)-O(9)	146.44(9)	O(8)-Tb(1)-O(11)	73.59(11)	O(5)-Dy(1)-O(8)	73.60(10)
O(12)-Gd(1)-O(9)	76.08(9)	O(9)-Tb(1)-O(11)	147.88(12)	O(18)-Dy(1)-O(8)	74.92(9)

3.2 Thermal Properties.

In order to characterize thermal stability of these complex, thermogravimetric analyses (TGA) of complex **1** were performed under nitrogen atmosphere (Fig. 2), the complex starts to decompose when the temperature raised to about 190 °C. Finally it was completely degraded into Gd₂O₃ when the temperature raised to 500 °C with

total loss of 82.2 wt% (calc 81.6 wt%). The TGA curve of **2**, **3** are similar to **1** (Fig. S1 Fig. S2) further indicate their isostructural architecture. The end product were characterized by X-ray powder diffraction (Fig. 2), the date is similar to the literature [29].

Fig. 2. TGA trace of complex **1** and the powder pattern of the end product

3.3 Magnetic properties

Variable-temperature magnetic susceptibilities of complexes **1**, **2** and **3** were measured from 300 K to 2 K in an applied field of 1 kOe. The $\chi_M T$ vs. T plots for **1** are shown in Fig. 3. At 300 K, the $\chi_M T$ value is $8.59 \text{ cm}^3 \text{ K mol}^{-1}$, close to the theoretical value $8.63 \text{ cm}^3 \text{ K mol}^{-1}$ (Uncoupled one Gd^{III} ion (f^7 electron configuration, $\chi_M T = 7.88 \text{ cm}^3 \text{ K mol}^{-1}$) plus two organic radical ($S = 1/2$, $\chi_M T = 0.375 \text{ cm}^3 \text{ K mol}^{-1}$)). Upon cooling, the $\chi_M T$ value of complex **1** increases slowly to a maximum of $9.68 \text{ cm}^3 \text{ K mol}^{-1}$ at about 20 K, then the value decreases to $8.82 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The increase of $\chi_M T$ from 300K to 20K indicates ferromagnetic interaction in the molecule when the temperature is relatively high while the decrease of $\chi_M T$ suggests the presence of antiferromagnetic interaction in the molecule when the temperature is relatively low.

Fig. 3. Temperature dependence of $\chi_M T$ for complex **1**. The solid lines represent the theoretical values based on the corresponding equations.

In order to evaluate the exchange coupling constants of complex **1**, considering Gd^{III} with an $^8S_{7/2}$ ground state, the magnetic interactions between Gd^{III} and the radicals can be well described by isotropic exchange interaction. Therefore the experimental data of complex **1** can be analyzed with an expression derived from a

spin Hamiltonian. For the tri-spin system, there are two kinds of magnetic interactions: Gd^{III}–radical (J_{Rad-Gd}) and radical–radical through the Gd^{III} ion ($J_{Rad-Rad}$) interactions. Considering the g value range of the radical and Gd^{III} ion, we assume that the radical and Gd^{III} ion have the same g value. Thus the variable-temperature magnetic susceptibilities data for complex **1** can be analyzed by a theoretical expression (Eq. (2)) deduced from a spin Hamiltonian (Eq. (1)).

$$H = -2J_{Rad-Gd} (\hat{S}_{Rad1} \cdot \hat{S}_{Gd} + \hat{S}_{Rad2} \cdot \hat{S}_{Gd}) - 2J_{Rad-Rad} \hat{S}_{Rad2} \cdot \hat{S}_{Rad1} \dots\dots\dots(1)$$

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \frac{A}{B}$$

$$A = 165 + 84 \exp\left(-\frac{9J_{Rad-Gd}}{kT}\right) + 84 \exp\left(-\frac{7J_{Rad-Gd} + 2J_{Rad-Rad}}{kT}\right) + 35 \exp\left(-\frac{16J_{Rad-Gd}}{kT}\right)$$

$$B = 5 + 4 \exp\left(-\frac{9J_{Rad-Gd}}{kT}\right) + 4 \exp\left(-\frac{7J_{Rad-Gd} + 2J_{Rad-Rad}}{kT}\right) + 3 \exp\left(-\frac{16J_{Rad-Gd}}{kT}\right) \dots\dots\dots(2)$$

The best fitting leads to $g = 1.96$, $J_{Rad-Gd} = 1.40 \text{ cm}^{-1}$, $J_{Rad-Rad} = -11 \text{ cm}^{-1}$ $R = 1.64 \times 10^{-5}$ where R is defined as $R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2 / \sum(\chi_M)_{obs}^2$ for complex **1**. The positive value of J_{Rad-Gd} indicates a weak ferromagnetic interaction between the Gd^{III} and the radicals in the molecule, and the negative $J_{Rad-Rad}$ indicates the antiferromagnetic interaction between the two intramolecular radicals. For complex **1**, these kinds of interactions were also observed in the similar Gd^{III}–Radical complexes [30–34].

Furthermore, the field dependence of magnetization of complex **1** has been determined at 2 K in the range of 0–70 kOe (Fig. 3). Upon increasing in the applied field, M increases up to $7.85 N\beta$ at 70 kOe, which is much smaller than the saturation value of $9.0 N\beta \text{ mol}^{-1}$ for parallel arrangement of Gd^{III} and radical spins of $S = 9/2$ in the case of one Gd^{III} and two radical ferromagnetically coupled. At the lower fields the magnetization is below the magnetization calculated with the Brillouin function for noncoupled $S = 7/2$ and two $S = 1/2$ spin centers ($g = 2.0$, $T = 2 \text{ K}$). The result suggests the dominant antiferromagnetic coupling in **1**, which is similar to other reported radical-Gd-radical compounds [38].

The $\chi_M T$ values of **2** and **3** at 300 K are $12.69 \text{ cm}^3 \text{ K mol}^{-1}$ and $14.96 \text{ cm}^3 \text{ K mol}^{-1}$ respectively (Fig. 4) close to the theoretical value $12.57 \text{ cm}^3 \text{ K mol}^{-1}$ and $15.08 \text{ cm}^3 \text{ K mol}^{-1}$ for an uncoupled system for one Ln^{III} ion (Tb^{III}: 7F_6 , $g = 3/2$, $C = 11.82 \text{ cm}^3 \text{ K mol}^{-1}$) and Dy^{III}: $^6H_{15/2}$, $S = 5/2$, $L = 5$, $g = 4/3$, $C = 14.17 \text{ cm}^3 \text{ K mol}^{-1}$) plus two organic radical ($S = 1/2$, $0.375 \text{ cm}^3 \text{ K mol}^{-1}$). Upon cooling, for compound **2**, the $\chi_M T$ value increases to $25.26 \text{ cm}^3 \text{ K mol}^{-1}$ at 3 K, afterward the value decreases to $24.33 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. For compound **3**, the $\chi_M T$ value increases to $19.51 \text{ cm}^3 \text{ K mol}^{-1}$ at 3 K, afterward the value decreases to $16.73 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The increase of $\chi_M T$ indicates ferromagnetic interaction between the Ln^{III} and the radicals and the decrease of $\chi_M T$ suggests the presence of antiferromagnetic interaction between the two intramolecular radicals according to the results of the magnetic fitting of complex **1**.

Fig. 4. Temperature dependence of $\chi_M T$ for complexes **2** (left) and **3** (right).

The field dependences of magnetizations for **2** and **3** have been determined at 2 K in the range of 0–70 kOe (Fig. 5). Upon increasing in the applied field, M increases up to 5.79 and 7.71 $N\beta$ at 70 kOe for **2** and **3** respectively, which does not reach the saturation values, indicating the presence of a magnetic anisotropy and/or low-lying excited states in the system.

Fig. 5. Field dependence of magnetization of **2** and **3** at 2.0 K.

Alternating current (ac) susceptibility measurements for complex **2** were carried out in low temperature regime under a zero dc field to investigate the dynamics of the magnetization. As shown in Fig. 6 complex **2** exhibits weak frequency dependent out-of-phase signals. Such a behavior suggests occurrence of relaxation mechanism like quantum tunneling of the magnetization (QTM). As is known, the tunneling mechanism can be suppressed by applying a static magnetic field. Thus the ac susceptibilities are measured in 3 kOe external field for the Tb compound to remove the degeneracy of the levels on opposite sides of the anisotropy barrier. As expected, zero-field QTM is partially suppressed and out-of-phase frequency-dependent signals are more visible (Fig. 7) the peaks of out-of-phase signals are visible and the relaxation time τ data derived from the χ'' peaks follow the Arrhenius law $\tau = \tau_0 \exp(\Delta_\tau/k_B T)$ where $\tau = 1/2\pi f$. The pre-exponential factor $\tau_0 = 1.59 \times 10^{-9}$ s and the effective anisotropy barrier $\Delta_\tau/k_B = 22.79$ K (Fig. 8). The obtained values of τ_0 and Δ are comparable to those of reported SMMs [29,37,38].

Fig. 6. Temperature dependence of the in-phase (left) and out-of-phase (right) components of ac susceptibility for **2** in zero dc field.

Fig. 7. Temperature dependence of the in-phase (left) and out-of-phase (right) components of ac susceptibility for **2** in a 3 KOe dc field.

Fig. 8. Plot of $\ln(\tau)$ versus T^{-1} fitting to the Arrhenius law for complex **2**.

Alternating current (ac) susceptibility measurements for complex **3** were carried out in low temperature regime under a zero dc field to investigate the dynamics of the magnetization. As shown in Fig. S3 there are no obvious frequency dependent out-of-phase signals. We do not think that complex **3** express SMM behavior at low temperature. This may be due to the small energy barrier which could not prevent the inversion of the spin.

The crystal field created by the surrounding ligands significantly influences the local anisotropy of Ln^{III} ions, which plays an important role in the slow magnetization relaxations. As in this work, the center Ln^{III} ions in similar LnO_8 coordination

environments. However complex **2** shows field-induced SMM behavior, while complex **3** does not exhibit any signals in the out-of-phase ac magnetic susceptibility. Considering the Kramers' nature of Dy^{III} ions, the double degeneracy of the ground state, $\pm m_J$, is always ensured in zero applied dc field [42]. The absence of slow magnetization relaxation might mostly result from the small energy gap between the ground state and the first-excited state in certain local symmetry.

4. Conclusion

In this paper, we have successfully obtained three lanthanide-radical complexes. Single crystal X-ray analyses reveal that complexes **1**, **2** and **3** are isomorphous, the center Ln ions are eight-coordinated. The frequency dependence of the ac magnetic susceptibility studies reveal that Tb complex show the presence of frequency-dependent signals at low temperature indicating that it behaves as single-molecular magnet.

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Appendix A. Supplementary data

CCDC ID: 1026107, 1026108, 993800 contain the supplementary crystallographic data for complex **1**, **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] O. Kahn, Molecular Magnetism, VCH, New York, 1993.
- [2] M.L. Kahn, J.P. Sutter, S. Golhen, P. Guionneau, L. Ouahab, O. Kahn, D. Chasseau, J. Am. Chem. Soc. 122 (2000) 3413.
- [3] P. Zhang, Y.N. Guo, J.K. Tang, Coord. Chem. Rev. 257 (2013) 1728.
- [4] M.J. Graham, J.M. Zadrozny, M. Shiddiq, J.S. Anderson, M.S. Fataah, S. Hill, D.E. Freedman, J. Am. Chem. Soc. 136 (2014) 7623.
- [5] A. Mailman, S.M. Winter, J.W.L. Wong, C.M. Robertson, A. Assoud, P.A. Dube, R.T. Oakley, J. Am. Chem. Soc. 137 (2015) 1044.
- [6] L. Chatelain, J.P.S. Walsh, J. Pecaut, F. Tuna, M. Mazzanti, Angew. Chem. Int. Ed. 53 (2014) 13434.
- [7] D. Ruiz-Molina, M. Mas-Torrent, J. Gómez, A.I. Balana, N. Domingo, J. Tejada, M.T.

- Martinez, C. Rovira, J. Veciana, *Adv. Mater.* 15 (2003) 38.
- [8] M. Clemente-León, H. Soyer, E. Coronado, C. Mingotaud, C.J. Gómez-García, P. Delhaès, *Angew. Chem. Int. Ed.* 37 (1998) 2842.
- [9] S. Moller, C. Perlov, W. Jackson, C. Taussig, S.R. Forrest, *Nature* 426 (2003) 166
- [10] W. Liang, M. P. Shores, M. Bockrath, J. R. Long and H. Park, 417 *Nature* (2002) 725.
- [11] L. Bogani, W. Wernsdorfer, *Nat. Mater.* 7 (2008) 179.
- [12] P. Zhang, L. Zhang, C. Wang, S. Xue, S. Y. Lin, J. Tang, *J. Am. Chem. Soc.* 136 (2014) 4484.
- [13] J.L. Liu, J.Y. Wu, Y.C. Chen, V. Mereacre, A.K. Powell, L. Ungur, L.F. Chibotaru, X. M. Chen, M.L. Tong, *Angew. Chem. Int. Ed.* 53 (2014) 12966.
- [14] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Novak, *Angew. Chem. Int. Ed.* 40 (2001) 1760.
- [15] L. Bogani, C. Sangregorio, R. Sessoli and D. Gatteschi, *Angew. Chem. Int. Ed.* 44 (2005) 5817.
- [16] K. Bernot, J. Luzon, L. Bogani, M. Etienne, C. angregorio, M. Shanmugam, A. Caneschi, R. Sessoli, D. Gatteschi, *J. Am. Chem. Soc.* 131 (2009) 5573.
- [17] L. Chatelain, J.P.S. Walsh, J. Pecaut, F. Tuna, M. Mazzanti, *Angew. Chem. Int. Ed.* 53 (2014) 13434.
- [18] P. Zhang, L. Zhang, C. Wang, S. Xue, S.Y. Lin, J. Tang, *J. Am. Chem. Soc.* 136 (2014) 4484.
- [19] G. Poneti, K. Bernot, L. Bogani, A. Caneschi, R. Sessoli, W. Wernsdorfer, D. Gatteschi, *Chem. Commun.* (2007) 1807
- [20] J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *J. Am. Chem. Soc.* 133 (2011) 14236.
- [21] J. D. Rinehart, M. Fang, W. J. Evans, J. D. Rinehart, M. Fang, W. J. *Nat. Chem.* 538 (2011) 538.
- [22] E.T. Chernick, R. Casillas, J. Zirzmeier, D.M. Gardner, M. Gruber, H. Kropp, K. Meyer, M. R. Wasielewski, D.M. Guldi, R.R. Tykwinski, *J. Am. Chem. Soc.* 137 (2015) 857.
- [23] A. Mailman, S.M. Winter, J. W. Wong, C.M. Robertson, A. Assoud, P.A. Dube, R..T. Oakley, *J. Am. Chem. Soc.* 137 (2015) 1044.
- [24] M. Zhu, P. Hu, Y. Li, X. Wang, L. Li, D. Liao, V.M.L.D.P. Goli, S. Ramasesha, J.P. Sutter, *Chem. Eur. J.* 20 (2014) 13356.
- [25] Z.X. Wang, X. Zhang, Y.Z. Zhang, M.X. Li, H. Zhao, M. Andruh, K.R. Dunbar, *Angew. Chem. Int. Ed.* 53 (2014) 11567.
- [26] L.B.L. Escobar, G.P. Guedes, S. Soriano, N.L. Speziali, A.K. Jordao, A. Cunha, V.F. Ferreira, C. Maxim, M. A. Novak, M. Andruh, M.G.F. Vaz, *Inorg. Chem.* 53 (2014) 7508.
- [27] E.F. Ullman, J.H. Osiecki, D.G.B. Boocock, R. Darcy, *J. Am. Chem. Soc.* 94 (1972) 7049.
- [28] G.M. Sheldrick, (1997) SHELXS-97: Program for the Solution of Crystal Structures, University of Göttingen, Germany
- [29] R.K. Tamrakar, D.P. Bisen, I.P. Sahu, K. Upadhyay, M. Sahu, *J. Disp. Technol.* 12 (2016) 921.
- [30] P. Hu, C. Zhang, Y. Gao, Y. Li, Y. Ma, L. Li, D. Liao, *Inorg. Chim. Acta.* 398 (2013) 136.
- [31] A. Okazawa, T. Ishida, *Inorg. Chem.* 49 (2010) 10144.
- [32] M. Baskett, A.P. Filho, N.F. Oliveira, J.A. Chandrasekaran, J.T. Mague, P.M. Lahti, *Inorg. Chem.* 50 (2011) 5060.
- [33] Y. Gao, Y. Wang, P. Hu, M. Yang, Y. Ma, Q. Wang, L. Li, D. Liao, *Inorg. Chem. Comm.* 27

- (2013) 31.
- [34] C.-X. Zhang, X.-M. Qiao, Y.-K. Kong, B. Wang, Y.-Y. Zhang, Q.-L. Wang, *J. Mol. Struct.* 1081 (2015) 348.
- [35] E. Coronado, S. C. Gimenez, F. M. Romero, *Inorg. Chem.* 48 (2009) 2205.
- [36] W. J. Evans, D.G. Giarikos, M.A. Johnston, M.A. Greci, J.W. Ziller, *J. Chem. Soc. Dalton Trans* (2002) 520.
- [37] N. Zhou, Y. Ma, C. Wang, G.F. Xu, J.K. Tang, J.X. Xu, S.P. Yan, P. Cheng, L.C. Li, D.Z. Liao, *Dalton Trans.* (2009) 8489.
- [38] L.L. Li, S. Liu, Y. Zhang, W. Shi, P. Cheng, *Dalton Trans.* 44 (2015) 6118.
- [39] C.X. Zhang, H.W. Chen, W.M. Wang, Y.Y. Zhang, *Inorg. Chem. Commun.* 24 (2012) 177.
- [40] F.-X. Du, P. Hu, Y.Y. Gao, F.-P. Xiao, Y.N. Wu, *Inorg. Chem. Comm.* 48 (2014) 166.
- [41] X.F. Wang, P. Hu, Y.G. Li, L.C. Li, *Chem. Asian. J.* 10 (2015) 325.
- [42] J.D. Rinehart, J.R. Long, *Chem. Sci.* 2 (2011) 2078.

Graphical abstract

Three lanthanide–nitronyl nitroxide complexes: syntheses, crystal structures and magnetic properties

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One nitronyl nitroxide radical and its three mononuclear tri-spin compounds have been successfully prepared. The magnetic studies reveal that Tb complex displays frequency-dependent signals at low temperature suggesting that it behaves as SMM.

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1. Three lanthanide-radical complexes.
2. Complexes **1**, **2** and **3** are isomorphous
3. Ferromagnetic interactions between Ln – Radical.
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