

Syntheses, crystal structures and magnetic properties of three lanthanide-nitronyl nitroxide complexes[†]

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Abstract: Three new lanthanide-nitronyl nitroxide radical complexes were successfully synthesized with the formula of $[\text{Ln}(\text{hfac})_3(\text{PyNONIT})_2]$ (Ln=Dy (**1**), Tm (**2**), Ho (**3**)). All the complexes were isostructural and crystallized in $C2/c$ space group, in which the central metal ions were eight-coordinated in slightly distorted square antiprism coordination geometries (D_{4d} symmetry). Magnetic studies indicated the existence of antiferromagnetic interaction in complexes **1–3**.

Keywords: lanthanide complex; nitronyl nitroxide radical; magnetic properties; crystal structure; rare earths

In recent years, single-molecule magnets (SMMs) have attracted great attentions for their potential applications in the field of molecular spintronics, magnetic refrigeration, high-density magnetic memories and quantum computing devices^[1–6]. With the vigorous development of SMMs, the lanthanide-based SMMs have also gained extensive concerns for their large spin ground states and unquenched orbital momentums that can generate strong magnetic anisotropy, especially dysprosium complexes are the most useful motifs for the large moment and high anisotropy of the Dy^{III} ion ($^6\text{H}_{15/2}$, $S=5/2$, $L=5$ and $J=15/2$)^[7]. In addition to the adoption of proper lanthanide metal ions, combining the nitronyl nitroxide radicals with lanthanide ions makes a promising way to construct complexes with desired magnetic properties^[8,9] because the nitronyl nitroxide radicals can be act as spin carriers and transmit magnetic exchange interactions^[10–13].

The radical ligand 2-(4'-oxidopyridyl)-4,4,5,5-tetramethylimidazolin-1-oxyl-3-oxide (PyNONIT) has been successfully synthesized and a series of Dy and Tb-radical complexes were also obtained in our previous work^[14,15]. Aiming to make a further research on the magnetic properties of lanthanide complexes based on PyNONIT ligand, three lanthanide ions (Ln=Dy, Tm, Ho) were chosen to construct new complexes via tuning chemical methods. As a coligand in the reaction system, hexafluoroacetylacetonate is still used to keep a charge balance and complete the coordination environments around metal ions.

Herein, three lanthanide-radical complexes were re-

ported with the formula of $[\text{Ln}(\text{hfac})_3(\text{PyNONIT})_2]$ (Ln=Dy (**1**), Tm (**2**), Ho (**3**)) and structurally studied in detail. Magnetic studies for complexes **1–3** were also performed and the results indicated the existence of antiferromagnetic interaction in complexes **1–3**.

1 Experimental

1.1 Materials and measurements

All chemicals applied to the syntheses were of analytical grade and used without further purification. $\text{Ln}(\text{hfac})_3 \cdot 2\text{H}_2\text{O}$ were synthesized according to the method in literature^[16]. The radical ligand named PyNONIT was also prepared by the reported approach^[17].

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. Single-crystal X-ray diffraction measurements of complexes **1–3** were performed on an Oxford diffractometer SuperNova TM equipped with a graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071073$ nm) using the ω -scan technique. All of the crystal structures were solved by direct method and refined by full-matrix least-squares techniques based on F^2 using the SHELXS-97 and SHELXL-97 programs^[18,19]. Magnetic measurements were carried out on a Quantum Design MPMS XL-7 SQUID magnetometer. The diamagnetic corrections were estimated with Pascal's constants for all of the constituent atoms and the sample holders. The data collection, crystal parameters, and refinement results for complexes **1–3** are listed in Table 1.

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Table 1 Crystallographic data and structure refinement for complexes 1–3

Crystals	1	2	3
Formula	C ₃₉ H ₃₅ DyF ₁₈ N ₆ O ₁₂	C ₃₉ H ₃₅ F ₁₈ TmN ₆ O ₁₂	C ₃₉ H ₃₅ F ₁₈ HoN ₆ O ₁₂
<i>M</i> /(g/mol)	1284.23	1290.66	1286.66
<i>T</i> /K	121(3)	121(3)	121(3)
Wavelength/nm	0.071073	0.071073	0.071073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> /nm	3.1922(2)	2.93824(7)	2.94841(12)
<i>b</i> /nm	1.17468(8)	1.17086(3)	1.17228(3)
<i>c</i> /nm	1.39006(8)	1.38915(4)	1.38876(6)
α /°	90.00	90.00	90.00
β /°	113.665(5)	94.520(2)	94.665(4)
γ /°	90.00	90.00	90.00
Volume/nm ³	4.7741(5)	4.7642(2)	4.7842(3)
<i>Z</i>	4	4	4
Cal. density/(mg/m ³)	1.787	1.799	1.786
μ	1.701	1.999	1.790
<i>F</i> (000)	2540.0	2552.0	2544.0
θ range/°	5.28 to 50.02	4.84 to 50.02	4.82 to 50.02
<i>R</i> _{int}	0.0534	0.0345	0.1060
Data/restraints/parameters	4217/306/391	4195/0/348	4212/300/455
GOOF	1.082	1.037	1.052
Final <i>R</i> indices	<i>R</i> ₁ =0.0813,	<i>R</i> ₁ =0.0515,	<i>R</i> ₁ =0.0586,
[<i>I</i> ≥2σ(<i>I</i>)]	<i>R</i> ₂ =0.2050	<i>R</i> ₂ =0.1319	<i>R</i> ₂ =0.1497
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0934,	<i>R</i> ₁ =0.0549,	<i>R</i> ₁ =0.0615,
	<i>R</i> ₂ =0.2213	<i>R</i> ₂ =0.1352	<i>R</i> ₂ =0.1539
Residual map/(10 ³ e/nm ³)	5.17/−1.70	1.92/−1.68	4.06/−1.32

1.2 Syntheses of [Ln(hfac)₃(PyNONIT)₂] (Ln=Dy (1), Tm (2), Ho (3))

A stirred solution of Ln(hfac)₃·2H₂O (0.04 mmol) in 30 mL heptane was heated to reflux for 2 h at 110 °C and then cooled to 90 °C, whereafter, PyNONIT (0.08 mmol) in 3 mL dichloromethane was added. The resulting solution was stirred for 10 min, then cooled to room temperature and filtered. Green clubbed crystals were obtained after two days. Yield: 35%, 30% and 40% based on Ln(hfac)₃·2H₂O for 1–3, respectively. Anal. calcd (%) for C₃₉H₃₅DyF₁₈N₆O₁₂ (**1**): C 36.44, H 2.74, N 6.54. Found: C, 36.76, H, 3.02, N, 6.09; Anal. calcd (%) for C₃₉H₃₅TmF₁₈N₆O₁₂ (**2**): C 36.29, H 2.73, N 6.51. Found: C, 36.64, H, 3.08, N, 6.85; Anal. calcd (%) for C₃₉H₃₅HoF₁₈N₆O₁₂ (**3**): C 36.41, H 2.74, N 6.53. Found: C, 36.53, H, 3.14, N, 6.34.

2 Results and discussion

2.1 Description of crystal structures

Single-crystal X-ray diffraction data reveal that lan-

thanide complexes 1–3 are isostructural and crystallize in monoclinic crystal system with the space group *C2/c* and all the three complexes display radical-Ln(III)-radical tri-spin structures. Herein, only the crystal structure of **2** will be described in detail. Complex **2** consists of one Tm^{III} ion, two PyNONIT ligands and three hfac[−] anions (Fig. 1), its asymmetric unit are composed by half of the whole mononuclear structure in **2**. The coordination sphere of Tm1 is completed by eight oxygen atoms, two coordinated oxygen atoms come from two PyNONIT ligands and the remaining oxygen atoms come from three hfac[−] anions. The geometry around Tm^{III} ion in the mononuclear complex shows a slightly distorted square antiprism (*D*_{4d} symmetry) with the Tm1–O bond lengths in the range of 0.2282(4)–0.2349(4) nm, and the angles of O–Tm1–O are in the range of 72.14(18)–146.50(17)°, respectively (Fig. 2). The nitronyl nitroxide radicals as monodentate ligands to Tm^{III} ion with N2–O6 and N3–O5 bond lengths in the five membered ring are 1.2838(0) and 0.12579(0) nm, respectively. However, the coordinated N1–O1 bond length in the pyridine ring is 0.13307(0) nm, which is in the range of N–O bond length of tri-spin radical-Ln(III)-radical complexes^[20,21]. As shown in Fig. 3, the 3D packing structures of complex **2**

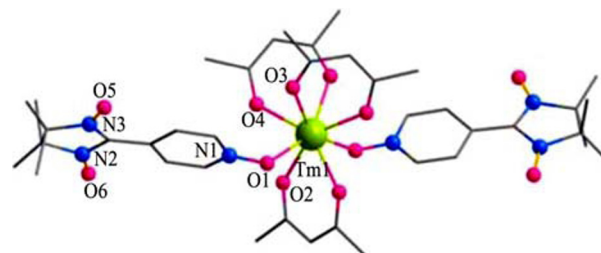


Fig. 1 Crystal structure of **2** (Color code: Tm, light green; C, grey; N, blue; O, mauve. Fluorine, hydrogen, and some carbon atoms are omitted for clarity)

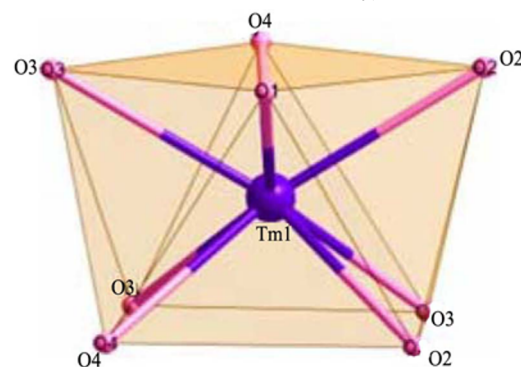


Fig. 2 Polyhedron of Tm atom for **2**

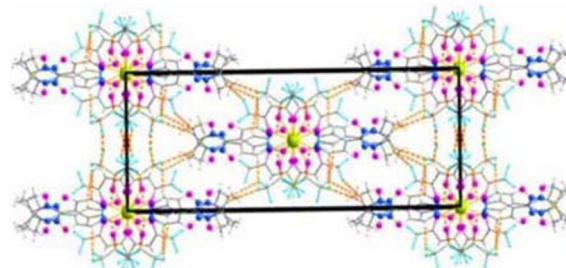


Fig. 3 3D packing diagram of **2**

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