三个镧系金属氮氧自由基配合物的合成、结构及磁性

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摘要：以氮氧自由基为配体,合成了 3 例氮氧自由基–稀土三自旋单核配合物[Ln(hfac)₃(NIT-Ph-4-Br)₂](Ln=Gd(**1**), Tb(**2**), Dy(**3**), hfac=六氟乙酰丙酮,NIT-Ph-4-Br=4,4,5,5-四甲基-2-(4′-溴)-咪唑啉-3-氧化-1-氧基自由基。单晶结构分析表明 3 个配合物均属单斜晶系 $P2_1/c$ 空间群,配合物中的 Ln(Ⅲ)离子为八配位模式,并且拥有相似的自由基–稀土–自由基单核结构。对配合物的磁性测试结果表明,配合物 **1** 中自由基与 Gd(Ⅲ)离子之间存在着铁磁相互作用,自由基与自由基之间存在着反铁磁相互作用；配合物 **2**,**3** 中,稀土离子与自由基之间存在弱的反铁磁相互作用

关键词：氮氧自由基；稀土；晶体结构；磁性
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Three Lanthanide Nitronyl Nitroxide Radical Compounds: Synthesises, Structures and Magnetic Properties

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Abstract: Three lanthanide-nitronyl nitroxide radical compounds [Ln(hfac)₃(NIT-Ph-4-Br)₂] (Ln=Gd(**1**), Tb(**2**), Dy (**3**), hfac =hexafluoroacetylacetonate, NIT-Ph-4-Br =2-(4′-bromide)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide) have been successfully prepared and characterized by single crystal X-ray diffraction, IR spectroscopy and elemental analyses. Single crystal X-ray crystallographic analyses reveal that all these three compounds are isostructural and crystallize in the $P2_1/c$ space group, which are composed of one Ln (hfac)₃ unit and two NIT-Ph-4-Br radicals. Magnetic studies reveal that ferromagnetic interactions and antiferromagnetic interactions coexist in Gd complex and there are very weak ferromagnetic interactions between Ln(Ⅲ) ions and the coordinated nitronyl nitroxide in Tb complex and Dy complex. CCDC: 1496095, **1**; 1496096, **2**; 1496097, **3**.

Keywords: nitronyl nitroxide radical; lanthanides; crystal structure; magnetic properties

0 Introduction

Molecular magnetic materials have attracted scientists attention in the past two decades due to their potential applications in high-density magnetic memories, quantum computing devices and molecular spintronics [1-6]. Among the different approaches to prepare molecular magnetic materials the metal-radical strategy that consists of matching paramagnetic organic molecules with transition metal complex gives rise to a variety of compounds with different structural and magnetic dimensionalities. Up to now various organic paramagnetic molecules such as verdazyl, semiquinone and nitronyl nitroxide (NIT) radicals have been widely studied in the field of molecular magnetism[7-14]. Among them, nitronyl nitroxide radicals have received noteworthy attention because this type of radicals can act as bidentate ligands with identical N-O coordination groups. Besides, nitronyl nitroxide family of radicals are relatively stable and easy to obtain derivatives with substituents containing donor atoms. However, NIT radicals are poorly donating ligands, thus utilization of strong electron withdrawing coligands such as hexafluoroacetylacetonate (hfac)[15-17] and trifluoroacetylacetonate (tfac)[18-20] in the metal to improve weak coordination ability is necessary. The steric demand of hfac or tfac restrict the dimensionality of the resulting metal-radical complex. Thus numbers of zero- and one-dimensional complexes were prepared by this strategy. Recently lanthanide ions based molecular magnetic materials have been extensively studied because lanthanide ions such as terbium(Ⅲ) and dysprosium(Ⅲ) are good candidates for the construction of SMMs due to their significant magnetic anisotropy arising from the large, unquenched orbital angular momentum[21-24].

To further study the magnetic properties of NIT radical-lanthanide compounds, in this paper we report a nitronyl nitroxide radical (Scheme 1) and its corresponding Ln-nitronyl nitroxide compounds [Ln(hfac)₃(NIT-Ph-4-Br)₂] (Ln=Gd(**1**), Tb(**2**), Dy(**3**), hfac=hexafluoroacetylacetonate, NIT-Ph-4-Br=2-(4′-bromine phenyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide), their crystal structures and magnetic properties were described in detail.
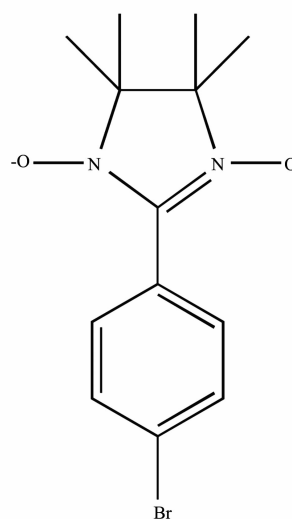
Scheme 1 Molecular structure of NIT-Ph-4-Br

1 Experimental

1.1 Materials and measurements

All reagents and solvents were purchased from Aladdin and used without further purification. The radical ligand NIT-Ph-4-Br was synthesized according to literature [25]. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Nicolet IS10 IR spectrometer using KBr pellets in the range of 4 000~500 cm^{-1}. The magnetic measurements were carried out with MPMSXL-7 SQUID magnetometer. Diamagnetic corrections were made with Pascals constants for all the constituent atoms.

1.2 Synthesis of complex 1

A suspension of Gd(hfac)₃·2H₂O (0.05 mmol) in 15 mL dry boiling heptane was heated to reflux for about 1 h. Then the solution was cooled to 65 ℃, a solution of NIT-Ph-4-Br 0.1 mmol) in 2 mL of CHCl₃ was added. The resulting solution was stirred for about 2 min and then cooled to room temperature. The filtrate was allowed to stand at room temperature for slow evaporation. Slow evaporation of the final solution for about four days yielded dark-blue block crystals suitable for single-crystal X-ray analysis. Yield: 43.5% based on rare-earth. Elemental analysis calculated for C₄₁H₃₅Br₂GdF₁₈N₄O₁₀ (%): C: 35.10; H:

2.51; N: 3.99. Found (%): C: 33.88; H: 2.79; N: 4.12. FTIR (KBr, cm^{-1}) : 1 656(s), 1 527(w), 1 385(w), 1 350 (w), 1 255(s), 1 198(s), 1 096(s), 796(w), 660(w).

1.3　Synthesis of Complex 2

Complex **2** was synthesized using the same procedure for complex **1** with Tb(hfac)$_3$·2H$_2$O instead of Gd(hfac)$_3$·2H$_2$O. Yield: 47.9%. Elemental analysis calculated for C$_{41}$H$_{35}$Br$_2$TbF$_{18}$N$_4$O$_{10}$ (%): C: 35.06; H: 2.51; N: 3.99. Found (%): C: 35.69; H: 2.57; N: 4.11. FTIR (KBr, cm^{-1}): 1 655(s), 1 599(w), 1 528(w), 1 399(w), 1 352(w), 1 255(s), 1 199(s), 1 096(w), 797(w), 660(w).

1.4　Synthesis of Complex 3

Complex **3** was synthesized using the same procedure for complex **1** with Dy(hfac)$_3$·2H$_2$O instead of Gd(hfac)$_3$·2H$_2$O. Yield: 42.9%. Elemental analysis calculated for C$_{41}$H$_{35}$Br$_2$DyF$_{18}$N$_4$O$_{10}$ (%): C: 34.97; H: 2.51; N: 3.98. Found (%): C: 34.91; H: 2.77; N: 3.87 (%). FTIR (KBr, cm^{-1}): 1 655(s), 1 600(w), 1 527(w), 1 399(w), 1 352(w), 1 255(s), 1 199(s), 1 096(w), 798 (w), 662(w).

1.5　X-ray Crystallographic Study

The crystal structure data of complexes **1**, **2** and **3** were collected using a Rigaku Saturn CCD diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation (λ =0.071 073 nm). Crystal size of complexes **1**, **2** and **3** are 0.15 mm ×0.12 mm × 0.11 mm, 0.17 mm×0.11 mm×0.10 mm, 0.12 mm× 0.11 mm×0.10 mm respectively. The structures were solved by the direct methods with SHELXS-97[26] and refined by full-matrix least-squares methods on F^2 with SHELXL-97 program package [27]. 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. The details of the crystal parameters, data collection, and refinements for these complexes were listed in Table 1 and 2.

CCDC: 1496095, **1**; 1496096, **2**; 1496097, **3**.

Table 1　Crystal data and structure refinement for 1, 2 and 3

Complex	1	2	3
Empirical formula	C$_{41}$H$_{35}$Br$_2$F$_{18}$GdN$_4$O	C$_{41}$H$_{35}$Br$_2$F$_{18}$TbN$_4$	C$_{41}$H$_{35}$Br$_2$F$_{18}$DyN$_4$O
Formula weight	1 402.80	1 404.47	1 408.05
T / K	296	296	173
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / nm	1.966 1(1)	1.980 3(8)	1.947 2(7)
b / nm	1.261 7(8)	1.262 4(5)	1.237 1(5)
c / nm	2.271 2(2)	2.288 5(10)	2.257 6(8)
β / (°)	106.177(2)	105.584(5)	104.750(2)
V / nm^3	2.756(2)	2.731(4)	2.728(4)
Z	4	4	4
D_c / (g·cm^{-3})	1.640	1.609	1.664
μ / mm^{-1}	1.325	1.377	1.493
R_{int}	0.035 9	0.075 1	0.054 1
$F(000)$	2 740	2 744	1 366
Reflections collected	39 438	46 085	23 418
Independent reflections	9 410	9 461	9 822
GOF on F^2	0.972	1.025	1.004
$R_1{}^a$ [$I>2\sigma(I)$]	0.045 6	0.065 2	0.029 4
$wR_2{}^b$ [$I>2\sigma(I)$]	0.131 4	0.153 3	0.062 6

$^a R_1=\sum (\| F_o|-|F_c \|)/ \sum |F_o|$; $^b wR_2 =[\sum w(F_o{}^2-F_c{}^2)^2/ \sum w(F_o)^2]^{1/2}$

**Table 2　Selected bond lengths (nm) and angles (°) for 1 , 2 and 3**

1					
Gd(1)-O(5)	0.234 6(4)	Gd(1)-O(7)	0.238 7(3)	N(3)-O(2)	0.130 7(5)
Gd(1)-O(2)	0.235 1(4)	Gd(1)-O(9)	0.239 9(4)	N(4)-O(1)	0.126 4(6)
Gd(1)-O(10)	0.236 8(3)	Gd(1)-O(8)	0.240 1(4)	N(2)-O(3)	0.129 9(6)
Gd(1)-O(3)	0.236 9(4)	Gd(1)-O(6)	0.240 7(4)	N(1)-O(4)	0.126 0(7)
O(5)-Gd(1)-O(2)	98.67(14)	O(5)-Gd(1)-O(3)	95.23(15)	O(5)-Gd(1)-O(7)	72.57(13)
O(5)-Gd(1)-O(10)	136.36(13)	O(2)-Gd(1)-O(3)	137.69(13)	O(2)-Gd(1)-O(7)	71.97(11)
O(2)-Gd(1)-O(10)	98.31(13)	O(10)-Gd(1)-O(3)	98.59(13)	O(10)-Gd(1)-O(7)	151.07(12)
2					
Tb(1)-O(8)	0.233 8(5)	Tb(1)-O(9)	0.237 2(5)	N(4)-O(4)	0.131 7(8)
Tb(1)-O(2)	0.235 0(6)	Tb(1)-O(6)	0.237 6(5)	N(3)-O(3)	0.129 1(8)
Tb(1)-O(4)	0.235 2(5)	Tb(1)-O(5)	0.239 4(5)	N(1)-O(1)	0.127 2(9)
Tb(1)-O(10)	0.236 3(5)	Tb(1)-O(7)	0.239 4(5)	O(2)-N(2)	0.130 4(8)
O(8)-Tb(1)-O(2)	95.7(2)	O(8)-Tb(1)-O(10)	137.50(19)	O(8)-Tb(1)-O(9)	73.3(2)
O(8)-Tb(1)-O(4)	98.3(2)	O(2)-Tb(1)-O(10)	97.9(2)	O(2)-Tb(1)-O(9)	73.5(2)
O(2)-Tb(1)-O(4)	137.74(19)	O(4)-Tb(1)-O(10)	98.04(19)	O(4)-Tb(1)-O(9)	148.72(19)
3					
Dy(1)-O(7)	0.233 0(2)	Dy(1)-O(5)	0.236 6(2)	O(9)-N(2)	0.130 5(3)
Dy(1)-O(9)	0.233 9(2)	Dy(1)-O(8)	0.238 3(2)	O(2)-N(3)	0.130 6(3)
Dy(1)-O(2)	0.234 5(2)	Dy(1)-O(3)	0.238 5(2)	O(10)-N(1)	0.127 3(3)
Dy(1)-O(4)	0.235 5(2)	Dy(1)-O(6)	0.238 6(2)	O(1)-N(4)	0.127 5(4)
O(7)-Dy(1)-O(9)	99.00(8)	O(7)-Dy(1)-O(4)	136.64(8)	O(7)-Dy(1)-O(5)	71.44(8)
O(7)-Dy(1)-O(2)	95.20(9)	O(9)-Dy(1)-O(4)	98.41(8)	O(9)-Dy(1)-O(5)	71.50(8)
O(9)-Dy(1)-O(2)	137.56(8)	O(2)-Dy(1)-O(4)	98.09(8)	O(2)-Dy(1)-O(5)	75.65(8)

2　Results and discussion

2.1　Crystal structures of complexes 1~3

　　As is shown in Fig.1, Compound **1** is a mononuclear coordination compound crystallizing in the monoclinic space group $P2_1/c$ with $Z =4$. The central Gd (Ⅲ) ion is eight coordinated in slightly distorted triangular dodecahedral GdO_8 geometry completed by two non-bridged NO groups from two separate organic radicals and three bischelate hfac⁻ anions. The distances of Gd-O bonds range from 0.235 6(4) to 0.240 7(4) nm. The coordinated N(3)-O(2)
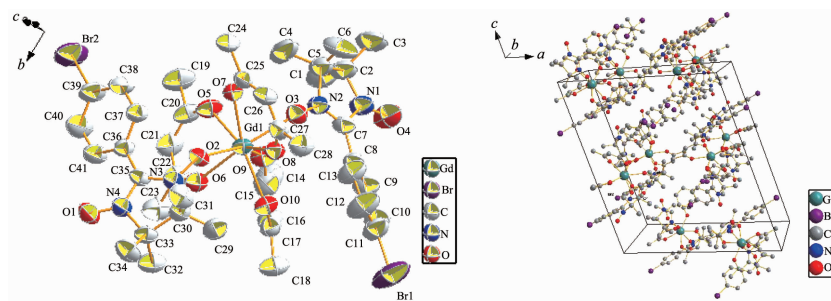
All hydrogen atoms and fluorine atoms are omitted for clarity

Fig.1 Molecular structure (left) with thermal ellipsoids drawn at 30% probability and crystal packing diagram(right) of complex **1**

and N(2)-O(3) bond lengths of nitronyl nitroxide radicals are 0.130 7(5) nm and 0.129 9(6) nm respectively and the uncoordinated N(4)-O(1) and N(1)-O(4) bond lengths are 0.126 4(6) nm and 0.126 0(7) nm respectively, which are comparable to those of reported tri-spin radical-Ln(Ⅲ)-radical complexes[28-33]. The nearest Gd⋯Gd distance between adjacent molecules is 1.071 6(5) nm (Fig.1).

Compound **2** is isostructural to compound **1** and the bond lengths of Tb-O are in the range of 0.233 8(5)~ 0.239 4 (5) nm, which are a little bit shorter than the bond lengths of Gd-O. The nearest Tb⋯Tb distance between adjacent molecules is 1.081 2(4) nm.

Compound **3** is also isostructural to compound **1** and the bond lengths of Dy-O are in the range of 0.233 0(2)~0.238 6(2) nm, which are a little bit shorter

than the bond lengths of Gd-O and Tb-O. The nearest Dy⋯Dy distance between adjacent molecules is 1.060 8(3) nm.

2.2 Magnetic property of complex 1

The temperature dependence of the magnetic susceptibilities **1**, **2**, and **3** were measured from 300 to 2.0 K in an applied field of 1 kOe, and the magnetic behaviors of complex **1** are shown in Fig.2. At 300 K, the $\chi_M T$ value is 8.61 cm^3·K·mol^{-1}. The values are in good agreement with the theoretical value of 8.63 cm^3·K·mol^{-1} (uncoupled one Gd(Ⅲ) ion (f^7 electron configuration, $\chi_M T$ =7.88 cm^3·K·mol^{-1}) plus two organic radicals (S =1/2, $\chi_M T$ =0.375 cm^3·K·mol^{-1})). Upon cooling, the $\chi_M T$ value of complex **1** increase steadily to a maximum of 10.03 cm^3·K·mol^{-1} at 13.9 K, afterward decreases to 9.13 cm^3·K·mol^{-1} at 2.0 K.
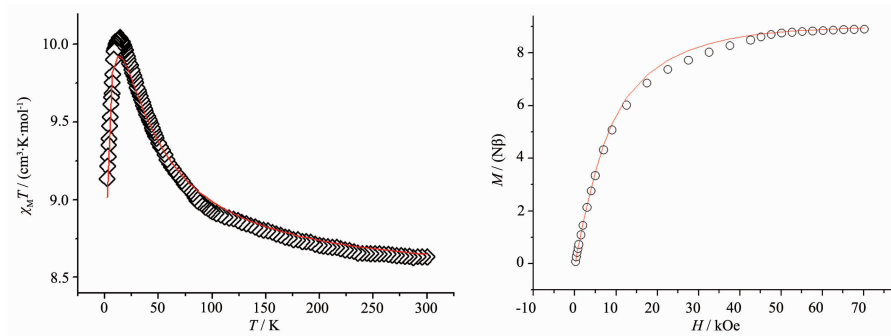
Left: The solid lines represent the theoretical values based on the corresponding equations; Right: the solid line represents the theoretical curve for the sum of the Brillouin function for one Gd(Ⅲ) (S=7/2) and two radical (S=1/2) with g=2

Fig.2　Temperature dependence of $\chi_M T$(left) and field dependence of magnetization at 2.0 K (right) for complex **1**

There are two kinds of magnetic interactions in this radical-Gd(Ⅲ)-radical complex at the same time. The first one is Gd(Ⅲ)-radical interaction and the second one is radical-radical interaction.

The magnetic interactions between Gd(Ⅲ) and the radicals can be described by isotropic exchange interaction. Therefore the experimental data for complex **1** can be analyzed with an expression derived from a spin Hamiltonian. 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 susceptibility data for complex **1** can be analyzed by a theoretical expression (Eq.(**2**)) deduced from a spin Hamiltonian (Eq.(**1**)). The J_{Rad-Gd} represent the magnetic coupling for

the Gd-radical and $J_{Rad-Rad}$ for radical-radical, and the zJ' in Eq.(**2**) representing the intermolecular interactions.

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

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

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

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

$$\chi_{total} = \frac{\chi_M}{1-\frac{zJ'}{Ng^2B^2}\chi_M} \quad (2)$$

The best fitting results give coupling parameters g=1.99, J_{Rad-Gd}=2.81 cm^{-1}, $J_{Rad-Rad}$=−10.85 cm^{-1}, zJ'=−0.02 cm^{-1}, R=1.64×10^{-5}, where R is defined as R=($\chi_{M,obs}$−$\chi_{M,calc}$)^2/($\chi_{M,obs}$)^2 for complex **1**. The positive value of J_{Rad-Gd} indicates that there is a weak ferromagnetic interaction between the Gd(Ⅲ) and the radicals in the molecule. The negative $J_{Rad-Rad}$ indicates the antiferromagnetic interaction between the two intramolecular radicals. It is worth noting that the value of zJ' is much smaller than that of $J_{Rad-Rad}$. The obtained J value is comparable with the previously reported Gd(Ⅲ)-radicals compounds[28-34].

Furthermore, the field dependence of magnetization of complex **1** has been determined at 2 K in the range of 0~70 kOe (Fig.2). Upon increasing in the applied field, M increases up to 8.87$N\beta$ at 70 kOe, which corresponds well to the value expected for a ground state with a spin multiplicity of S=9/2 in the case of one Gd(Ⅲ) and two radical ferromagnetically coupled. At the lower fields the value is smaller than the magnetization calculated with the Brillouin function for noncoupled S=7/2 and two S=1/2 spin centers (g=2.0, T=2 K), which suggests the dominant

antiferromagnetic interaction between the Gd(Ⅲ) ion and the coordinated NIT radical.

2.3 Magnetic properties of complex 2 and complex 3

While for complex **2** (Fig.3), at 300 K, the $\chi_M T$ value is 12.46 cm^3·K·mol^{-1}, and the values are in good agreement with to the theoretical value 12.57 cm^3·K·mol^{-1} in uncoupled system of one Tb(Ⅲ) ion (f^9 electron configuration, $\chi_M T$=11.82 cm^3·K·mol^{-1}) and two organic radical (S=1/2, $\chi_M T$=0.375 cm^3·K·mol^{-1}). Upon cooling, the $\chi_M T$ values of complex **2** maintain a constant behavior down to about 50 K then the value decrease gradually and reach a minimum of 10.37 cm^3·K·mol^{-1}.

Complex **3** shows similar magnetic properties with complex **2**(Fig.3). At 300 K, the $\chi_M T$ value is 14.31 cm^3·K·mol^{-1}, close to the theoretical value of 14.92 cm^3·K·mol^{-1} (one Dy(Ⅲ) ion (f^9 electron configuration, $\chi_M T$=14.17 cm^3·K·mol^{-1}) plus two organic radicals (S=1/2, $\chi_M T$=0.375 cm^3·K·mol^{-1})). Upon cooling, the $\chi_M T$ values of complex **3** maintain a constant behavior down to about 50 K then the value decrease gradually and reach a minimum of 8.21 cm^3·K·mol^{-1}.
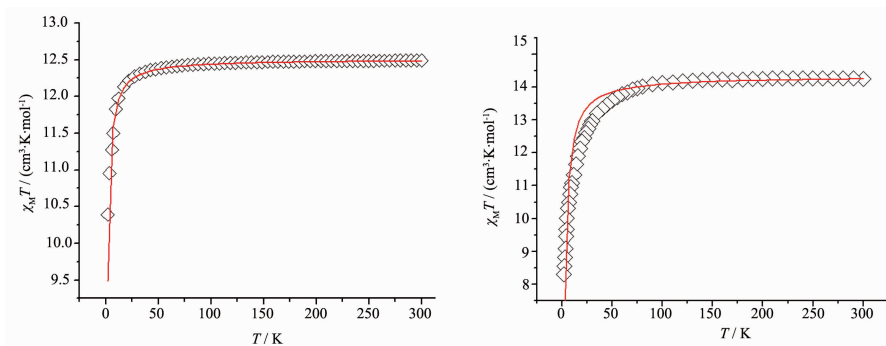
The solid lines represent the theoretical values based on the corresponding equations

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

There is no available expression to determine the magnetic susceptibilities of Ln(Ⅲ) systems with large anisotropy. To obtain a rough quantitative estimation of the magnetic interaction between Ln(Ⅲ) and radicals, the magnetic susceptibility χ_{total} of the complex can be assumed as the sum of χ_{Ln} of the isolated Dy(Ⅲ) or Tb(Ⅲ) ion and χ_{Rad} of the radical (Eq. (**4**)). The χ_{Tb} and χ_{Dy} can be described as Eq.(**5**) and

(**6**), respectively.

In the expression, Δ is the zero-field-splitting parameter, g is the Lande factor, k is the Boltzmann constant, β is the Bohr magneton constant and N is Avogadros constant. The zJ' parameter based on the molecular field approximation in Eq.(**7**) is introduced to simulate the magnetic interactions between all the paramagnetic species in the system. Thus the magnetic

data can be analyzed by the following approximate treatment of Eq. (4) ~(7) [29,31]. Giving the best fitting parameters for complex **2** are $g=1.49$, $\Delta=3.89\times10^{-2}$ cm^{-1}, $zJ'=1.63\times10^{-2}$ cm^{-1}, $R=1.12\times10^{-5}$ and for complex **3** are $g=1.36$, $\Delta=3.17\times10^{-2}$ cm^{-1}, $zJ'=2.14\times10^{-2}$ cm^{-1}, $R=1.92\times10^{-5}$, where R is defined as $R=(\chi_{M,obs}-\chi_{M,calc})^2/(\chi_{M,obs})^2$. The very small positive zJ' values are indicative of very

weak ferromagnetic interaction between Ln(Ⅲ) ions and the coordinated nitronyl nitroxide, which is consistent with the reported heavy lanthanide-nitronyl nitroxide complexes.

$$\chi_{total} = \chi_{Ln} + 2\chi_{Rad} \tag{3}$$

$$\chi_M = \frac{Ng_{Rad}^2\beta^2}{3kT}\frac{1}{2}\left(\frac{1}{2}+1\right) \tag{4}$$

$$\chi_{Tb} = \frac{2Ng^2\beta^2}{kT}\frac{36\exp(\frac{-36\Delta}{kT})+25\exp(\frac{-25\Delta}{kT})+16\exp(\frac{-16\Delta}{kT})+9\exp(\frac{-9\Delta}{kT})+4\exp(\frac{-4\Delta}{kT})+\exp(\frac{\Delta}{kT})}{2\exp(\frac{-36\Delta}{kT})+2\exp(\frac{-25\Delta}{kT})+2\exp(\frac{-16\Delta}{kT})+2\exp(\frac{-9\Delta}{kT})+\exp(\frac{-4\Delta}{kT})+2\exp(\frac{-9\Delta}{kT})+1} \tag{5}$$

$$\chi_{Dy} = \frac{Ng^2\beta^2}{4kT}\cdot$$

$$\frac{225\exp(\frac{-225\Delta}{kT})+169\exp(\frac{-169\Delta}{kT})+121\exp(\frac{-121\Delta}{kT})+81\exp(\frac{-81\Delta}{kT})+49\exp(\frac{-49\Delta}{kT})+25\exp(\frac{-25\Delta}{kT})+9\exp(\frac{-9\Delta}{kT})+\exp(\frac{-\Delta}{kT})}{\exp(\frac{-225\Delta}{kT})+\exp(\frac{-169\Delta}{kT})+\exp(\frac{-121\Delta}{kT})+81\exp(\frac{-81\Delta}{kT})+\exp(\frac{-49\Delta}{kT})+\exp(\frac{-25\Delta}{kT})+\exp(\frac{-9\Delta}{kT})+\exp(\frac{-\Delta}{kT})} \tag{6}$$

$$\chi_M = \frac{\chi_{total}}{1-[2zJ'/(Ng^2\beta^2)]\chi_{total}} \tag{7}$$

The field dependences of magnetizations for complexes **2** and **3** have been determined at 2 K in the range of 0~70 kOe (Fig.4). Upon increasing in the applied field, M increases up to $5.87N\beta$ and $7.73N\beta$ at 70 kOe for **2** and **3**, respectively, which is much lower than the saturation value of $11.0N\beta$ (one Tb(Ⅲ) ion with $g=3/2$ and $J=6$ $(9.0N\beta)$ plus two radicals with $g=2.0$ and $S=1/2$) and $12.0N\beta$ (one Dy(Ⅲ) ion with $g=4/3$ and $J=15/2$ $(10.0N\beta)$ plus two radicals with $g=2.0$ and $S=1/2$). Considering the strong spin-orbit coupling in Ln(Ⅲ) ions, the large gaps between experimental data and theoretical saturation values for compounds **2** and **3** can be ascribed to the presence of a magnetic anisotropy and/or low-lying excited states in the system.

2.4　Dynamic magnetic properties for 2 and 3

Alternating current (ac) susceptibility measurements for **2** and **3** were carried out in the low temperature region under a zero dc field with frequency of 111 and 511Hz. The result (Fig.5) shows that there are no obvious frequency dependent in-
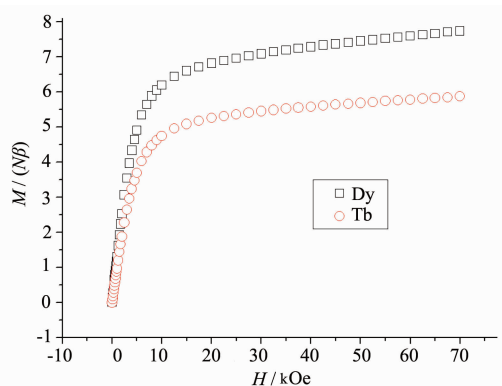

Fig.4　Field dependence of magnetization of **2** and **3** at 2.0 K
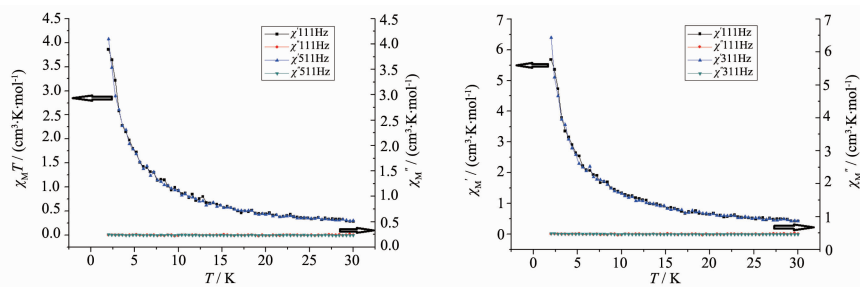

Fig.5　Temperature dependence of the in-phase and out-of-phase components of ac susceptibility for **2**(left) and **3**(right) in zero dc field with an oscillation of 3.5 Oe

phase（χ'）and out-of-phase（χ''）signals for both complex **2** and **3**, they do not express SMMs behavior at low temperature.

3　Conclusions

In conclusion, we report three new complexes based on nitronyl nitroxide radicals and lanthanide ions. These three compounds have similar structures, in which two radical ligands are coordinated to the Ln(Ⅲ) ions via the oxygen atoms of the nitroxide to form the three spin system. The magnetic studies reveal that ferromagnetic interactions (between the intramolecular Ln and radical) and antiferromagnetic interactions (between the intramolecular radicals) coexist in complex **1**. Complexes **2** and **3** show very weak ferromagnetic interaction between Ln(Ⅲ) ions and the coordinated nitronyl nitroxide. Both complex **2** and **3** do not have SMMs behavior at low temperature, this may due to the small energy barrier which could not prevent the inversion of spin.

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