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含氮氧自由基的 Gd,Tb,Dy 配合物的合成、结构及磁性

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摘要: 合成了一个新颖的氮氧自由基配体, 并用该配体合成了 3 例未见文献报道的氮氧自由基–稀土三自旋单核配合物 Ln(hfac)$_3$(NIT-Ph-4-OCHCH$_3$CH$_3$)$_2$(Ln=Gd(**1**), Tb(**2**), Dy(**3**); hfac=六氟乙酰丙酮; NIT-Ph-4-OCHCH$_3$CH$_3$=4,4,5,5-四甲基-2-(4′-异丙氧基苯基)–咪唑啉-3-氧化-1-氧基自由基)。单晶结构分析表明配合物 **1**、**2**、**3** 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自由基与稀土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。

关键词: 氮氧自由基; 稀土; 晶体结构; 磁性
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Gd(Ⅲ), Tb(Ⅲ) and Dy(Ⅲ) Complexes Based on a Nitronyl Nitroxide Radical: Syntheses, Structures and Magnetic Properties

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Abstract: One novel nitronyl nitroxide radical and its three mononuclear tri-spin compounds Ln(hfac)$_3$(NIT-Ph-4-OCHCH$_3$CH$_3$)$_2$ (Ln =Gd (**1**), Tb (**2**), Dy (**3**); hfac =hexafluoroacetylacetonate; NIT-Ph-4-OCHCH$_3$CH$_3$ =2-(4-isopropoxyphenyl)- 4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide) have been successfully prepared and characterized. Single crystal X-ray crystallographic analyses reveal that complexes **1**, **2**, and **3** shows similar radical-Ln(Ⅲ)-radical structures, which ar composed of one Ln(hfac)$_3$ units and two NIT-Ph-4-OCHCH$_3$CH$_3$ radicals. Magnetic studies reveal that ferromagnetic interactions (between intramolecular Ln and radical) and antiferromagnetic interactions (between the intramolecular radicals) are coexist in these complexes. CCDC: 985443, **1**; 1043098, **2**; 985444, **3**.

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

0 Introduction

Single-molecule m agnets (SMMs) have attracted many scientists attention in the past two decades[1-4]. 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) [5-7]. The SMMs have been found potential applications for the uses of high-density magnetic memories, magnetic refrigeration, quantum computing devices and spintronics at the molecular level[8-11]. Recently 4*f* metal ions were considered to be 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 4*f* metal ions based SMMs have been reported[12-17].

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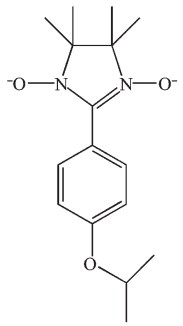
Apart from the choice of the metal ions, the ligand design also plays an important role. The use of organic radical ligands in the creation of new magnetic molecular compounds have attracted much attention since the discovery of the first radical-4*f* SMM by Gatteschis group [18]. As is well known, the stable radical ligands can generate typically stronger intramolecular magnetic exchange coupling. The strong exchange coupling between lanthanides and radicals generally leads to superior SMMs. Recently, a binuclear Tb(Ⅲ) complex bridged by a N_2^{3-} radical has been reported with a record blocking temperature of 13.9 K [19-20]. So far various organic radicals such as nitronyl nitroxide, verdazyl and semiquinone radicals have been reported[21-25]. However, researches are focused in particular on the nitronyl nitroxide (NIT) family of radicals, because these type of radicals are relatively stable and easy to obtain derivatives with substituents containing donor atoms. Nitronyl nitroxide radicals can act as bidentate ligands through their identical N-O coordination groups and give rise to complexes with different structures. Unfortunately, NIT radicals are poorly donating ligands, thus utilization of strong electron-withdrawing coligands such as hexafluoroacetylacetonate (hfac) and trifluoroacetylacetonate (tfac) are necessary. However, the steric demand of these coligands restrict the dimensionality of the resulting metal-radical compounds. So, it is easier to get zero- and one-dimensional compounds by this strategy.

To further study the magnetic properties of NIT radical-lanthanide compounds, in this paper we report a novel nitronyl nitroxide radical (Scheme 1) and its corresponding Ln-nitronyl nitroxide compounds Ln(hfac)$_3$(NIT-Ph-4-OCHCH$_3$CH$_3$)$_2$ (Ln=Gd (**1**), Tb (**2**), Dy (**3**); hfac =hexafluoroacetylacetonate; NIT-Ph-4-OCHCH$_3$CH$_3$ =2-(4-isopropoxyphenyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide), their crystal structures and magnetic properties were described in detail.



Scheme 1 Molecule structure of NIT-Ph-4-OCHCH$_3$CH$_3$

1 Experimental

1.1 Materials and physical measurements

All the starting chemicals were obtained from Aldrich and used without further purification. The radical ligand NIT-Ph-4-OCHCH$_3$CH$_3$ was prepared according to literature method[26]. Elemental analyses (C, H, N) were determined by Perkin-Elmer 240 elemental analyzer. The infrared spectra was recorded from KBr pellets in the range of 4 000~400 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 Pascals constants for all the constituent atoms.

1.2 Synthesis of Complex 1

A solution of Gd(hfac)$_3$·2H$_2$O (0.05 mmol) in 25 mL dry heptane was heated to reflux for 2 h. Then the solution was cooled to about 60 ℃, a solution of NIT-Ph-4-OCHCH$_3$CH$_3$ (0.1 mmol) in 2 mL of CH$_2$Cl$_2$ was added. The resulting solution was stirred for about 3 min and then cooled to room temperature. The filtrate was allowed to stand at room temperature for slow evaporation. After three days, some blue crystals were collected. Yield: 31.4 mg (45.5% based on Gd). Elemental analysis calculated for $C_{47}H_{49}F_{18}N_4O_{12}Gd$(%): C: 41.47; H: 3.63; N: 4.12. Found (%): C: 41.88; H: 3.69; N: 4.22.

1.3 Synthesis of Complex 2

Complex **2** was synthesized with the same procedure for complex **1** using Tb(hfac)$_3$·2H$_2$O instead of Gd(hfac)$_3$·2H$_2$O. Yield: 32.7 mg (47.9%). Elemental analysis calculated for $C_{47}H_{49}F_{18}N_4O_{12}Tb$ (%): C: 41.42; H: 3.62; N: 4.11. Found (%): C: 40.69; H: 3.57; N: 4.22.

1.4 Synthesis of Complex 3

Complex **3** was synthesized with the same procedure for complex **1** using Dy (hfac)$_3$·2H$_2$O instead of Gd(hfac)$_3$·2H$_2$O. Yield: 29.3 mg (42.9%). Elemental

analysis calculated for $C_{47}H_{49}F_{18}N_4O_{12}Dy$ (%): C: 41.31; H: 3.61; N: 4.10. Found(%): C: 40.91; H: 3.77; N: 4.17.

1.5 Crystal Structure Determination and Refinement

X-ray single-crystal diffraction data for complexes **1**, **2** and **3** were collected using a Rigaku Saturn CCD diffractometer at 113(2) K with Mo $K\alpha$ radiation (λ = 0.071 073 nm). The structure was solved by direct methods by utilizing the program SHELXS-97[27] and refined by full-matrix least-squares methods on F^2 with the use of the SHELXL-97 program package [28]. 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 and disorders were also observed for some fluorine atoms. Pertinent crystallographic data and structure refinement parameters for these complexes were listed in Table 1. Selected bond lengths and bond angles of complexes **1**, **2** and **3** are listed in Table 2.

CCDC: 985443, **1**; 1043098, **2**; 985444, **3**.

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

Complex	**1**	**2**	**3**
Empirical formula	$C_{47}H_{49}F_{18}Gd_1N_4O_{12}$	$C_{47}H_{49}F_{18}Tb_1N_4O_{12}$	$C_{47}H_{49}F_{18}Dy_1N_4O_{12}$
Formula weight	1 361.15	1 362.82	1 366.40
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a / nm	1.219 5(6)	1.987 2(4)	1.214 6(10)
b / nm	1.491 9(7)	1.255 6(3)	1.489 1(12)
c / nm	1.738 6(7)	2.282 1(5)	1.727 6(13)
α / (°)	98.890(5)	90	98.842(6)
β / (°)	103.057(5)	98.865(5)	102.753(6)
γ / (°)	111.943(3)	90	111.987(14)
V / nm^3	2.756(2)	2.731(4)	2.728(4)
Z	2	4	2
D_c / (g·cm^{-3})	1.640	1.609	1.664
μ / mm^{-1}	1.325	1.377	1.493
R_{int}	0.062 2	0.073 6	0.027 2
F(000)	1 362	2 728	1 366
Reflections collected	22 857	46 848	23 418
Independent reflections	9 649	9 876	9 822
GOF on F^2	1.017	1.032	1.021
R_1[a] [$I>2\sigma(I)$]	0.026 8	0.053 2	0.037 8
wR_2[b] [$I>2\sigma(I)$]	0.062 5	0.144 5	0.091 1

[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 distances (nm) and Angles (°) for 1 , 2 and 3

1					
Gd(1)-O(6)	0.233 0(8)	Gd(1)-O(7)	0.233 3(8)	O(2)-N(1)	0.127 1(3)
Gd(1)-O(3)	0.234 5(7)	Gd(1)-O(9)	0.235 0(8)	O(6)-N(3)	0.130 7(3)
Gd(1)-O(8)	0.252 9(8)	Gd(1)-O(12)	0.239 97(18)	O(3)-N(2)	0.130 4(2)
O(6)-Gd(1)-O(7)	93.24(7)	O(7)-Gd(1)-O(3)	105.83(7)	O(11)-Gd(1)-O(9)	148.80(6)
O(6)-Gd(1)-O(11)	102.93(7)	O(11)-Gd(1)-O(3)	88.67(7)	O(3)-Gd(1)-O(9)	73.27(6)

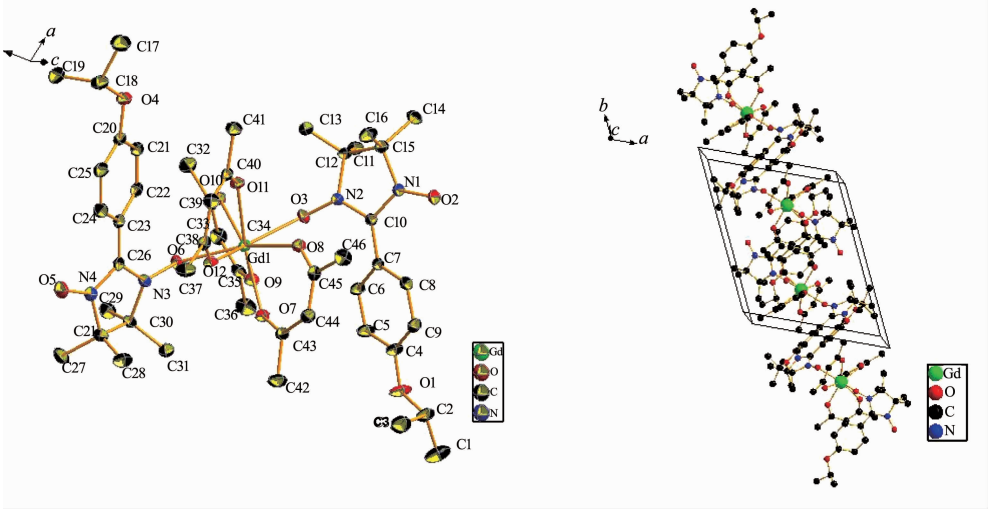
Continued Table 2

O(7)-Gd(1)-O(11)	136.79(6)	O(6)-Gd(1)-O(9)	76.52(6)	O(6)-Gd(1)-O(10)	69.66(7)
O(6)-Gd(1)-O(3)	137.62(6)	O(7)-Gd(1)-O(9)	73.74(6)	O(7)-Gd(1)-O(10)	145.23(6)
O(11)-Gd(1)-O(10)	77.69(6)	O(3)-Gd(1)-O(10)	73.46(6)		
			2		
Tb(1)-O(4)	0.234 0(3)	Tb(1)-O(11)	0.236 0(3)	O(5)-N(4)	0.127 4(5)
Tb(1)-O(2)	0.234 5(3)	Tb(1)-O(8)	0.237 4(3)	O(2)-N(2)	0.131 7(5)
Tb(1)-O(7)	0.234 6(3)	Tb(1)-O(12)	0.238 1(4)	N(3)-O(4)	0.131 7(5)
O(4)-Tb(1)-O(2)	137.10(12)	O(2)-Tb(1)-O(11)	103.35(12)	O(7)-Tb(1)-O(8)	72.69(13)
O(4)-Tb(1)-O(7)	103.62(13)	O(7)-Tb(1)-O(11)	137.94(12)	O(11)-Tb(1)-O(8)	74.01(12)
O(2)-Tb(1)-O(7)	90.96(13)	O(4)-Tb(1)-O(8)	75.98(12)	O(4)-Tb(1)-O(12)	149.61(12)
O(4)-Tb(1)-O(11)	92.38(13)	O(2)-Tb(1)-O(8)	146.60(12)	O(2)-Tb(1)-O(12)	73.00(12)
O(7)-Tb(1)-O(12)	74.68(13)	O(11)-Tb(1)-O(12)	72.28(13)		
			3		
Dy(1)-O(2)	0.232 1(3)	Dy(1)-O(8)	0.235 0(3)	O(4)-N(4)	0.126 9(4)
Dy(1)-O(9)	0.233 5(3)	Dy(1)-O(11)	0.235 1(3)	O(5)-N(3)	0.129 7(4)
Dy(1)-O(12)	0.234 6(3)	Dy(1)-O(5)	0.235 4(3)	O(2)-N(2)	0.130 4(5)
O(2)-Dy(1)-O(9)	92.77(11)	O(9)-Dy(1)-O(8)	136.97(11)	O(12)-Dy(1)-O(11)	74.09(11)
O(2)-Dy(1)-O(12)	69.99(12)	O(12)-Dy(1)-O(8)	76.91(12)	O(8)-Dy(1)-O(11)	149.09(11)
O(9)-Dy(1)-O(12)	145.80(11)	O(2)-Dy(1)-O(11)	76.58(12)	O(2)-Dy(1)-O(5)	137.83(11)
O(2)-Dy(1)-O(8)	103.30(12)	O(9)-Dy(1)-O(11)	73.22(11)	O(9)-Dy(1)-O(5)	105.91(12)
O(12)-Dy(1)-O(5)	73.72(11)	O(8)-Dy(1)-O(5)	88.47(12)		

2 Results and discussion

2.1 Crystal Structure of Complex 1

Single-crystal X-ray diffraction analyses reveal that all these three compounds show similar radical-Ln(Ⅲ)-radical structures, which are composed of one $Ln(hfac)_3$ unit and two NIT-Ph-4-$OCHCH_3CH_3$ radicals. Compounds **1** and **3** are isostructural and crystallize in the $P\bar{1}$ space group, while compound **2** crystallizes in the $P2_1/c$ space group.



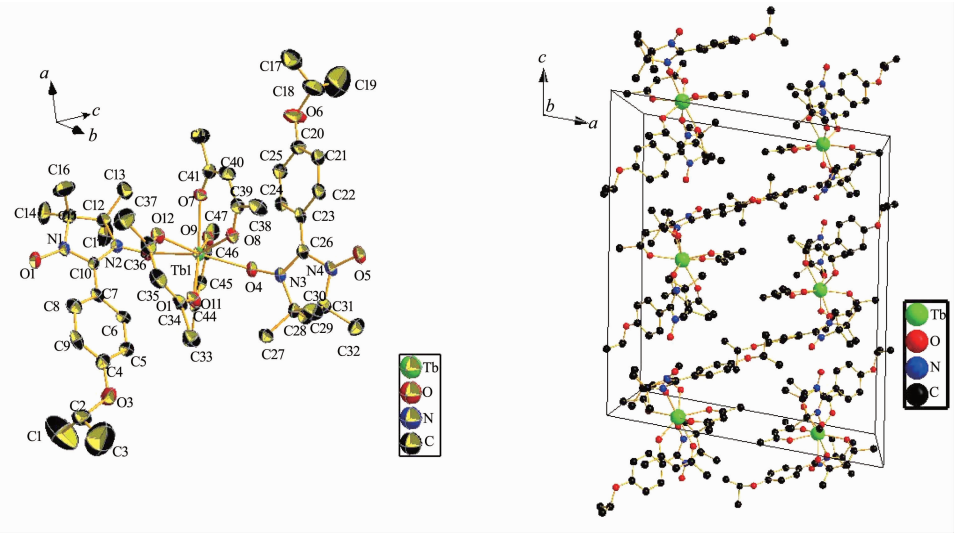
Thermal ellipsoids are drawn at 30% probability; All hydrogen atoms and fluorine atoms are omitted for clarity

Fig.1 Molecular structure (left) and crystal packing diagram of complex **1** (right)

In complex **1**, the central Gd(Ⅲ) ions are eight-coordinate with eight oxygen atoms. Two radical ligands bond to one Gd(Ⅲ) ion via the oxygen atoms of N-O coordination groups. The bond length of Gd(1)-O(6) is 0.234 8 nm while the bond length of Gd(1)-O(3) is 0.237 8 nm. The N(2)-O(3) and N(3)-O(6) bond lengths of nitronyl nitroxide radicals are 0.130 4 nm and 0.130 7 nm, respectively. The uncoordinated N(1)-O(2) and N(4)-O(5) bond lengths are 0.127 1 nm and 0.127 2 nm, respectively, which are comparable to those of reported tri-spin radical-Ln (Ⅲ)-radical complexes [29-35]. The other six oxygen atoms are from three hfacs with the Gd-O bond lengths in the range of 0.236 0~0.242 9 nm. The nearest Gd…Gd distance between the adjacent molecules is 1.024 9 nm (Fig.1).

2.2　Crystal structure of complex 2

The crystal structure of complex **2** shows that the central Tb(Ⅲ) ions are eight-coordinated with eight oxygen atoms. Two radical ligands bond to one Tb(Ⅲ) ion via the oxygen atoms of N-O coordination groups. The bond length of Tb(1)-O(4) is 0.234 1 nm while the bond length of Tb(1)-O(2) is 0.234 5 nm. The N(3)-O(4) and N(2)-O(2) bond lengths of nitronyl nitroxide radicals are 0.131 6 nm and 0.131 8 nm respectively. The uncoordinated N(1)-O(1) and N(4)-O(5) bond lengths are 0.128 3 nm and 0.127 3 nm, respectively, which are comparable to those of reported tri-spin radical-Ln (Ⅲ)-radical complexes [29-35]. The other six oxygen atoms are from three hfacs with the Tb-O bond lengths in the range of 0.234 6~0.241 7 nm. The nearest Tb … Tb distance between the adjacent molecules is 1.080 8 nm, which is a little bit longer than that for complex **1** (Fig.2).



Thermal ellipsoids are drawn at 30% probability; All hydrogen atoms and fluorine atoms are omitted for clarity

Fig.2　Molecular structure (left) and crystal packing diagram of complex **2** (right)

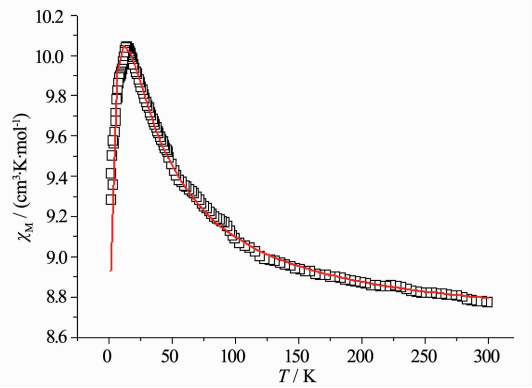
2.3　Crystal Structure of Complex 3

Compound **3** is isostructural to compound **1** and the bond lengths of Dy-O are in the range of 0.232 1~0.239 3 nm, which are a little shorter than the bond lenths of Gd-O.

2.4　Magnetic Properties of Complex 1

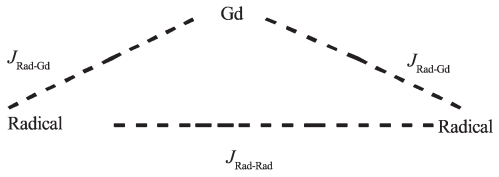
Variable-temperature magnetic susceptibilities of complexes **1**, **2**, and **3** were measured from 300 to 2.0 K in an applied field of 1 kOe. The $\chi_M T$ vs T plot for **1** are shown in Fig.3. At 300 K, the $\chi_M T$ value is 8.77 $cm^3 \cdot K \cdot mol^{-1}$, close to the theoretical value of 8.63 $cm^3 \cdot K \cdot mol^{-1}$ (Uncoupled one Gd(Ⅲ) ion, f^7electron configuration, $\chi_M T$=7.88 $cm^3 \cdot K \cdot mol^{-1}$) plus two organic radicals (S=1/2, $\chi_M T$=0.375 $cm^3 \cdot K \cdot mol^{-1}$)). Upon cooling, the $\chi_M T$ value of complex **1** increases steadily to a maximum of 10.04 $cm^3 \cdot K \cdot mol^{-1}$ at 15 K, afterward decreases to 9.28 $cm^3 \cdot K \cdot mol^{-1}$ at 2.0 K.

As shown in Scheme 2, there are two kinds of magnetic interactions in this radical-Gd (Ⅲ)-radical complex at the same time. The first one is Gd(Ⅲ)-



The solid lines represent the theoretical values based on the corresponding equations

Fig.3 Temperature dependence of $\chi_M T$ for complex **1**



Scheme 2 Model of intramolecular interactions

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. Thus 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**)[30-35].

The best fitting leads to g=2.00, J_{Rad-Gd}=2.57 cm^{-1}, $J_{Rad-Rad}$=−9.98 cm^{-1} 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. The obtained J value is comparable with the previously reported Gd^{Ⅲ}-radicals compounds[30-35].

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

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

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

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

2.5 Magnetic properties of complex 2

While for complex **2** (Fig.4), at 300 K, the $\chi_M T$ value is 13.08 cm^3·K·mol^{-1}, close 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}) plus two organic radical (S=1/2, $\chi_M T$=0.375 cm^3·K·mol^{-1}). Upon cooling, the $\chi_M T$ value of complex **2** increases steadily to a maximum of 28.62 cm^3·K·mol^{-1} at 3.0 K, afterward the value decreases to 28.54 cm^3·K·mol^{-1} at 2.0 K. The increase of $\chi_M T$ suggests the presence of ferromagnetic interaction between the Tb(Ⅲ) and the organic radical. The decrease of $\chi_M T$ at low temperature indicates the antiferromagnetic interaction between the two intramolecular radicals. The magnetic properties of complex **2** are similar to those of previously reported[29-35].

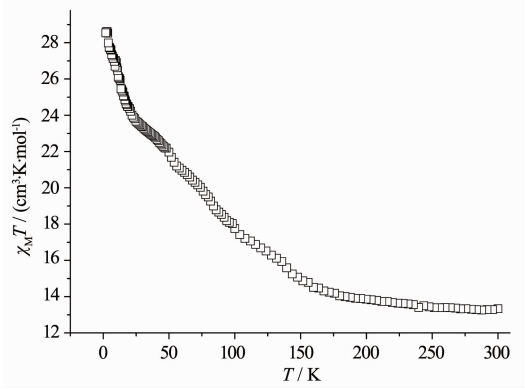


Fig.4 Temperature dependence of $\chi_M T$ for complex **2**

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.5, there are no obvious frequency dependent out-of-phase signals. We do not think that complex **2** express SMM behavior at low temperature. This may due to

the small energy barrier which could not prevent the inversion of spin.

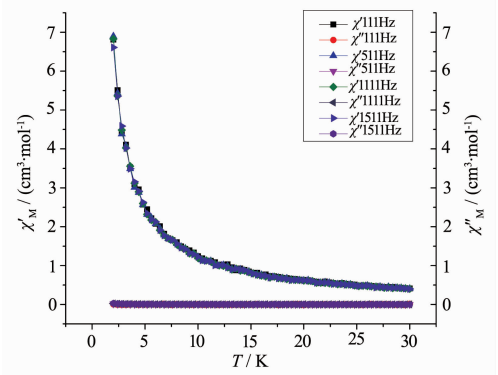


Fig.5　Temperature dependence of the in-phase and out-of-phase components of ac susceptibility for **2** in zero dc field with an oscillation of 3.5 Oe

2.6　Magnetic properties of complex 3

Complex **3** shows similar magnetic properties with complex **1** (Fig.6). At 300 K, the $\chi_M T$ value is 15.01 $cm^3 \cdot K \cdot mol^{-1}$, close to the theoretical value of 14.92 $cm^3 \cdot K \cdot mol^{-1}$. Upon cooling, the $\chi_M T$ value of complex **3** increases steadily to a maximum of 19.79 $cm^3 \cdot K \cdot mol^{-1}$ at 15.4 K, afterward decreases to 16.97 $cm^3 \cdot K \cdot mol^{-1}$ at 2.0 K. The plot also suggests the presence of ferromagnetic interaction between the Dy(Ⅲ) and the coordinated N-O groups of the organic radicals and the antiferromagnetic interaction between the two intramolecular radicals.

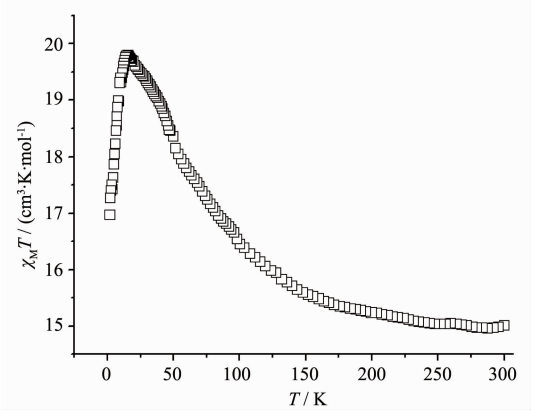


Fig.6　Temperature dependence of $\chi_M T$ for complexes **3**

Alternating current (ac) susceptibility measurements for complex **3** were also carried out in low temperature regime under a zero dc field. The result (Fig.7) shows that there are no obvious frequency dependent out-of-phase signals. Like complex **2**, complex **3** doesnt express SMMs behavior at low temperature.

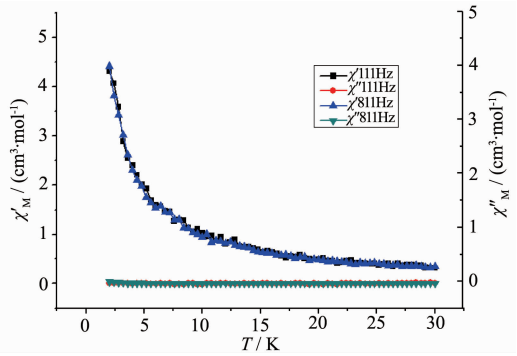


Fig.7　Temperature dependence of the in-phase and out-of-phase components of ac susceptibility for **3** in zero dc field with an oscillation of 3.5 Oe

3　Conclusions

A novel nitron yl nitroxide radical and its three corresponding mononuclear tri-spin compounds $Ln(hfac)_3(NIT\text{-}Ph\text{-}4\text{-}OCHCH_3CH_3)_2$ (Ln=Gd (**1**), Tb (**2**), Dy (**3**).) have been synthesized and characterized. The magnetic studies reveal that ferromagnetic interactions (between the intramolecular Ln and radical) and antiferromagnetic interactions (between the intramolecular radicals) are coexist in these complexes. Complexes **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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