

基于自由基配体的 Dy(III)配合物的设计、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 2 例未见文献报道的氮氧自由基-稀土配合物[Dy(hfac)₃(NIT-C₃H₅)(H₂O)]与[Dy(hfac)₃(NIT-C₃H₅)_n](hfac=六氟乙酰丙酮,NIT-C₃H₅=2-环丙烷基-4,4,5,5-四甲基-2-咪唑啉-3-氧化-1-氧基自由基)。单晶结构分析表明配合物 **1** 为单核结构,单斜晶系 *P*₂₁/*c* 空间群;配合物 **2** 为一维结构,单斜晶系 *P*₂₁/*c* 空间群。交流磁化率测试结果表明配合物 **2** 虚部表现出频率依赖,这表明配合物 **2** 是单链磁体。

关键词:氮氧自由基;镝;晶体结构;磁性

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Two Dy(III)-Radical Complexes: Synthesis, Structures and Magnetic Properties

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Abstract: Two Dy(III)-nitronyl nitroxide radical complexes [Dy(hfac)₃(NIT-C₃H₅)(H₂O)] and [Dy(hfac)₃(NIT-C₃H₅)_n](NIT-C₃H₅=2-cyclopropyl-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide, hfac=hexafluoroacetylacetonate), have been successfully prepared with different synthetic condition. Single crystal X-ray crystallographic analyses reveal that complex **1** is mononuclear complex which crystallize in the *P*₂₁/*c* space group while complex **2** is one-dimensional complex which crystallize in the *P*₂₁/*c* space group as well. Magnetic studies reveal that complex **2** exhibits frequency-dependence of ac magnetic susceptibilities, indicating that it behaves as single-chain magnet. CCDC: 1533515, **1**; 1533514, **2**.

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

0 Introduction

Recently, low-dimensional assemblies of anisotropic metal ions having zero- and one-dimensional structures that show magnetization relaxation have

attracted many scientists' attention^[1-5]. Such materials named as single chain magnets (SCMs) and single molecule magnets (SMMs). This type of materials are characterized as slow magnetization relaxation caused by the association of large ground state spin (*S*_g) value

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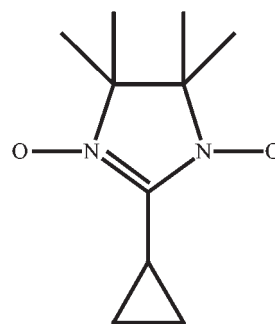
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with a significant uniaxial (Ising-like) magnetic anisotropy (D), which lead to a significant energy barrier to magnetization reversal (U)^[6-9]. The SCMs and SMMs have found potential applications in high-density information storage devices and quantum computers^[10-13]. Researchers so far are focused in particular on the $4f$ -based complexes 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 and SCMs have been reported^[14-18].

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 lead 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 $1/2$ ^[4]. Numbers SCMs and SMMs were prepared by this strategy^[17-18]. Among them metal-radical strategy that combining paramagnetic organic molecules with metal ions give rise to complexes with different structures and magnetic properties have been received more and more attention since the discovery of the first radical- $4f$ SMM by Gatteschi group^[19]. 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 N_2^{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^[22-28]. Nitronyl nitroxide (NIT) family of radicals are the most important type of radical ligand due to their 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 choose the nitronyl nitroxide radical NIT- C_3H_5 as ligand (NIT- C_3H_5 = 2-cyclopropyl-4,4,5,5-tetramethyl-



Scheme 1 NIT- C_3H_5

imidazoline-1-oxyl-3-oxide) (Scheme 1) to construct radical- $4f$ complex. Finally we have successfully prepared one zero-dimensional structure lanthanide-nitronyl nitroxide complex $[Dy(hfac)_3(NIT-C_3H_5)(H_2O)]$ and one one-dimensional structure lanthanide-nitronyl nitroxide complex $[Dy(hfac)_3(NIT-C_3H_5)]_n$ (hfac = hexafluoroacetylacetonate, NIT- C_3H_5 = 2-cyclopropyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide). Magnetic studies show that complex **2** shows the presence of frequency-dependent signals at low temperature suggesting that it behaves as SCMs.

1 Experimental

1.1 Materials and measurements

All the starting chemicals were obtained from Aldrich and used without further purification. The radical ligand NIT- C_3H_5 was prepared according to literature method^[29]. Elemental analyses (C, H, N) were determined by Perkin-Elmer 240 elemental analyzer. The infrared spectra were 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 Pascal's constants for all the constituent atoms.

1.2 Synthesis of $[Dy(hfac)_3(NIT-C_3H_5)(H_2O)]$ (1)

$Dy(hfac)_3 \cdot 2H_2O$ (0.081 9 g 0.1 mmol) was added to 25 mL *n*-heptane and heated to reflux for 0.5 h. The solution was cooled to 50 °C, then a solution of NIT- C_3H_5 (0.019 7 g 0.1 mmol) in CH_2Cl_2 (3 mL) was added and stirred for 1 min. The resulting mixture was cooled to room temperature filtrated then keep the solution in the fridge. The temperature was kept

between 2 to 5 °C for several days to give crystals suitable for X-ray analysis with a 52% yield. Anal. Calcd. for $C_{25}H_{22}F_{18}DyN_2O_9$ (%): C 30.05, H 2.22, N 2.80; Found (%): C 30.07, H 2.16, N 2.89. IR (KBr, cm^{-1}): 1 652(s), 1 499(s), 1 364(m), 1 262(s), 1 203(s), 1 149(s), 803(m), 663(m).

1.3 Synthesis of $[Dy(hfac)_3(NIT-C_3H_5)]_n$ (**2**)

$Dy(hfac)_3 \cdot 2H_2O$ (0.081 9 g 0.1 mmol) was added to 25 mL *n*-heptane and heated to reflux for 3 h. The solution was subsequently cooled to 70 °C, then a solution of NIT- C_3H_5 (0.019 7 g 0.1 mmol) in CH_2Cl_2 (3 mL) was added and stirred for 5 min. The solution was then cooled to room temperature, filtrated and the filtrate was evaporated at room temperature for several days to give crystals suitable for X-ray analysis, with a 47% yield. Anal. Calcd. for $C_{25}H_{20}F_{18}DyN_2O_8$ (%): C 30.06, H 2.05, N 2.85; Found (%): C 30.09, H 2.03, N 2.81. IR (KBr, cm^{-1}): 1 653(s), 1 502(s), 1 258(s), 1 201(s), 1 145(s), 802(m), 661(m).

1.4 X-ray crystallographic study

X-ray single-crystal diffraction data for complexes

1 and **2** were collected using a Rigaku Saturn CCD diffractometer at 293 K and 113 K, respectively, equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm). Crystal size of complexes **1** and **2** are 0.20 mm×0.20 mm×0.18 mm and 0.24 mm×0.2 mm×0.16 mm, respectively. The structures were solved by direct methods by using the program SHELXS-97^[30] and refined by full-matrix least-squares methods on F^2 with the use of the SHELXL-97^[31] 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 C and F atoms were observed for both complexes. The restraints of SPLIT, DELU and ISOR were applied for the three complexes to keep the disordered molecules reasonable. Pertinent crystallographic data and structure refinement parameters for complexes **1** and **2** were listed in Table 1 and 2.

CCDC: 1533515, **1**; 1533514, **2**.

Table 1 Crystal data and structure refinement for **1** and **2**

Complex	1	2
Empirical formula	$C_{25}H_{22}DyF_{18}N_2O_9$	$C_{25}H_{20}DyF_{18}N_2O_8$
Formula weight	998.95	980.93
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
<i>a</i> / nm	1.599 3(3)	1.084 6(2)
<i>b</i> / nm	1.413 0(3)	1.713 3(2)
<i>c</i> / nm	1.662 1(3)	1.835 7(3)
β / (°)	113.12(3)	97.895(2)
<i>V</i> / nm ³	3.454 3(12)	3.379 0(8)
<i>Z</i>	4	4
<i>D_c</i> / (g·cm ⁻³)	1.921	1.928
μ / mm ⁻¹	2.311	2.359
<i>R_{int}</i>	0.084 9	0.043 6
<i>F</i> (000)	1 944	1 904
Reflection collected	28 710	30 645
Independent reflection	6 063	5 915
GOF on <i>F</i> ²	1.009	1.027
<i>R</i> ₁ ^a [<i>I</i> >2σ(<i>I</i>)]	0.051 9	0.027 6
<i>wR</i> ₂ ^b [<i>I</i> >2σ(<i>I</i>)]	0.116 5	0.066 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 distances (nm) and angles ($^{\circ}$) for **1** and **2**

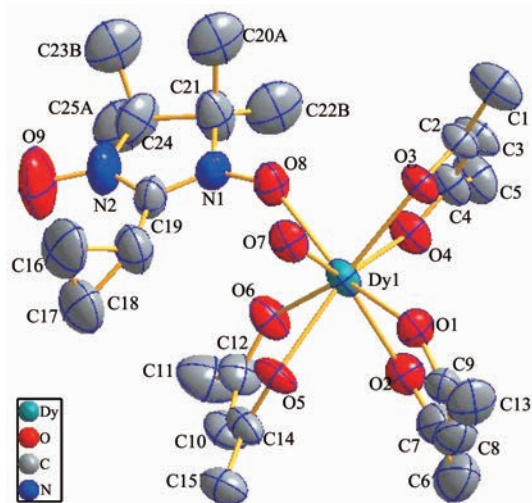
1					
Dy(1)-O(4)	0.224 3(5)	Dy(1)-O(6)	0.233 7(6)	O(8)-N(1)	0.130 3(8)
Dy(1)-O(7)	0.228 2(6)	Dy(1)-O(2)	0.234 5(7)	N(2)-O(9)	0.130 7(11)
Dy(1)-O(8)	0.230 5(6)	Dy(1)-O(5)	0.235 4(5)	N(1)-C(19)	0.132 1(10)
Dy(1)-O(1)	0.230 5(6)	Dy(1)-O(3)	0.245 4(5)	N(1)-C(21)	0.143 5(1)
O(4)-Dy(1)-O(7)	139.3(2)	O(4)-Dy(1)-O(1)	108.9(2)	O(4)-Dy(1)-O(6)	86.1(2)
O(4)-Dy(1)-O(8)	84.5(2)	O(7)-Dy(1)-O(1)	80.0(2)	O(7)-Dy(1)-O(6)	115.2(2)
O(7)-Dy(1)-O(8)	69.3(2)	O(8)-Dy(1)-O(1)	144.0(2)	O(8)-Dy(1)-O(6)	75.8(2)
2					
Dy(1)-O(3)	0.231 5(2)	Dy(1)-O(4)	0.234 7(2)	N(2)-O(7)	0.128 8(3)
Dy(1)-O(6)	0.232 3(2)	Dy(1)-O(2)	0.234 8 (2)	N(1)-O(8)	0.128 6(3)
Dy(1)-O(1)	0.233 7(2)	Dy(1)-O(5)	0.235 6(2)	N(1)-C(4)	0.132 9(4)
Dy(1)-O(8)a	0.233 9(2)	Dy(1)-O(7)	0.235 9(2)	N(1)-C(6)	0.149 2(4)
O(3)-Dy(1)-O(6)	138.42(7)	O(3)-Dy(1)-O(8)a	103.90(9)	O(3)-Dy(1)-O(4)	72.12(7)
O(3)-Dy(1)-O(1)	146.52(7)	O(6)-Dy(1)-O(8)a	89.22(9)	O(6)-Dy(1)-O(4)	74.50(7)
O(6)-Dy(1)-O(1)	74.79(7)	O(1)-Dy(1)-O(8)a	75.16(8)	O(1)-Dy(1)-O(4)	135.61(7)

Symmetry codes: a: $-x+1/2, y+1/2, -z+1/2$ for **2**.

2 Results and discussion

2.1 Crystal structure of complex 1

As shown in Fig.1, complex **1** crystallizes in the monoclinic space group $P2_1/c$. The central Dy(III) ions are eight-coordinated in square antiprism (D_{4d}) geometry (Table S1). Six oxygen atoms from three hfac molecules with the Dy-O bond lengths in the range of 0.226 0(6) ~ 0.245 4(5) nm. The other two oxygen atoms are from



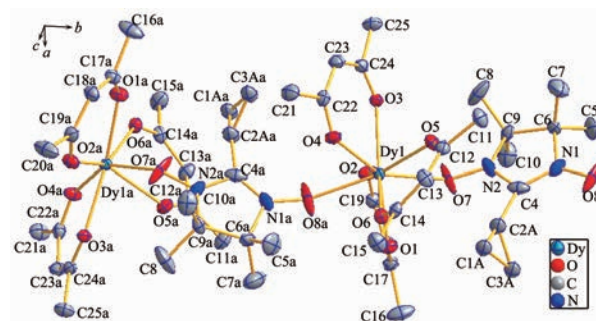
Thermal ellipsoids are drawn at 30% probability; All hydrogen atoms and fluorine atoms are omitted for clarity

Fig.1 Molecular structure of complex **1**

one radical molecule and one water molecule respectively. The bond length of Dy(1)-O(8)_{rad} is 0.230 7(3) nm and Dy(1)-O(7)_{water} is 0.228 6(5) nm. The nitronyl nitroxide radical act as monodentate ligand to Dy(III) ion through one N-O group, the N(1)-O(8) bond lengths are 0.129 8(9) nm while the uncoordinated N(2)-O(9) bond lengths are 0.129 9(12) nm, which are comparable to those of reported radical-Ln(III) complexes^[32-35].

2.2 Crystal structure of complex 2

As shown in Fig.2, complex **2** crystallizes in the monoclinic space group $P2_1/c$. The central Dy(III) ions are eight-coordinated in trigonal dodecahedron (D_{2d})



Thermal ellipsoids are drawn at 30% probability; All hydrogen atoms and fluorine atoms are omitted for clarity; Symmetry codes: a: $-x+1/2, y+1/2, -z+1/2$

Fig.2 Molecular structure of complex **2**

geometry (Table S2). Six oxygen atoms from three hfac molecules with the Dy-O bond lengths in the range of 0.231 4(2)~0.235 5(2) nm. The other two oxygen atoms are from two radical molecules with the Dy(1)-O(8) and Dy(1)-O(7) bond length of 0.234 1(3) nm and 0.236 1(3) nm, respectively. The nitronyl nitroxide radicals act as bridging ligands to Dy(III) ion through N-O group, the N(1)-O(8) and N(2)-O(7) bond lengths are 0.128 3(4) nm 0.128 6(4) nm, which are comparable to those of reported radical-Dy(III) complexes. Selected bond lengths and angles of complex **1** and **2** are listed in Table 2.

2.3 Magnetic properties of complex **1**

The temperature dependence of the magnetic susceptibilities **1** and **2** 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.3. At 300 K the $\chi_M T$ value of **1** is $12.32 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$. This value is close to the expected value $14.45 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ (uncoupled system of one Dy(III) ion (f^9 electron configuration, $\chi_M T=14.17 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$) plus one organic radical ($S=1/2, \chi_M T=0.375 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$)). Upon cooling,

the $\chi_M T$ value gradually decreases and reaches to the value of $11.13 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 18 K. Below 18 K, the $\chi_M T$ rapidly increases to $11.82 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 6 K then decreases on further cooling and reaches to the value of $11.46 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2.0 K. The decrease of $\chi_M T$ upon lowering of the temperature in the high-temperature range is most probably governed by depopulation of the Dy(III) Stark sublevels. The increase of $\chi_M T$ at low temperature suggests the presence of ferromagnetic interaction between the Dy(III) ions and the coordinated NO group of the organic radical.

The field dependences of magnetizations for complex **1** have been determined at 2 K in the range of 0~70 kOe (Fig.3). Upon increasing in the applied field M increases up to $7.02N\beta$ at 70 kOe, which does not reach the saturation values, indicating the presence of a magnetic anisotropy and/or low-lying excited states in the system, which corresponds to the reported results^[35]. The M value of a single Dy(III) in high applied field is usually around $5.23N\beta$ ^[36]. The experimental results revealing ferromagnetic interactions between Dy(III) and radical.

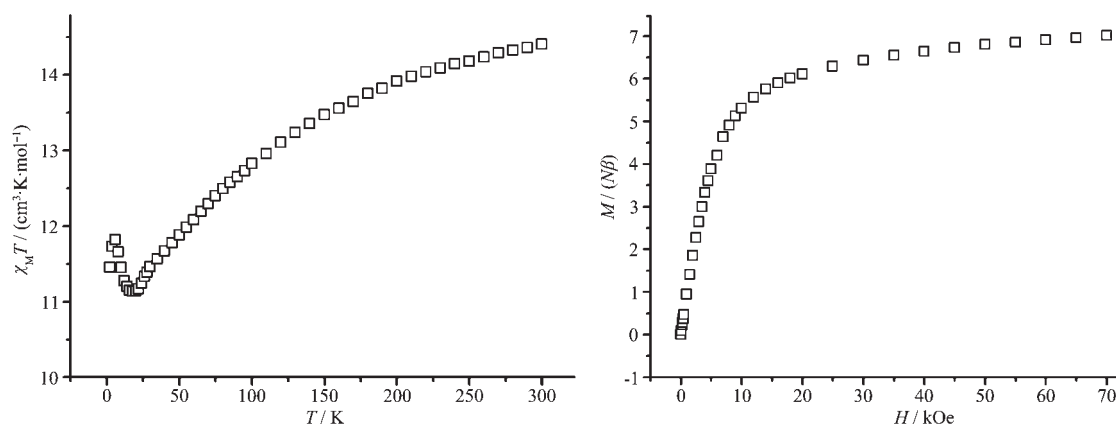


Fig.3 Temperature dependence of $\chi_M T$ for complex **1** (left) and field dependence of magnetization of **1** at 2.0 K (right)

Alternating current (ac) susceptibility measurements for complex **1** were carried out in low temperature regime under a zero dc field to investigate the dynamics of the magnetization. As shown in Fig.4 there are no obvious frequency dependent out-of-phase signals. We do not think that complex **1** express SMM behavior at low temperature. This may be due to the small energy barrier which could not prevent the inversion of spin.

2.4 Magnetic properties of complex **2**

For complex **2**, at 300 K, the $\chi_M T$ value is $14.58 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$. This value is close to the expected value of $14.45 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ (uncoupled system of one Dy(III) ion (f^9 electron configuration, $\chi_M T=14.17 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$) plus one organic radical ($S=1/2, \chi_M T=0.375 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$)). Upon cooling, the $\chi_M T$ value remains almost unchanged down to 50 K. Below this temperature, the $\chi_M T$ value decreases markedly and reaches a

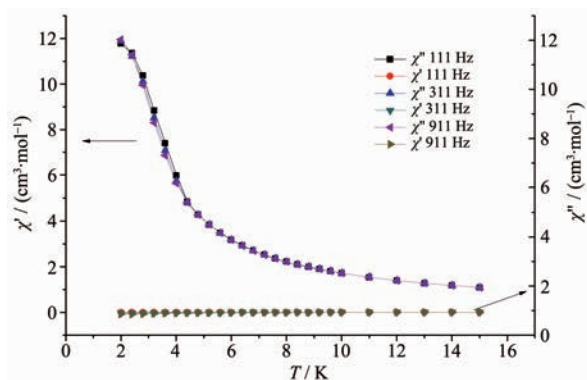


Fig.4 Temperature dependence of the in-phase and out-of-phase components of ac susceptibility for **1** in zero dc field with an oscillation of 3.5 Oe

value of $1.43 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2.0 K. For the present 1D magnetic system, both nearest-neighbor (NN) metal-radical magnetic coupling and next-nearest-neighbor (NNN) metal-metal or radical-radical magnetic interactions coexist. These NN exchange interactions are always ferromagnetic for heavy lanthanides, while the NNN interactions are always antiferromagnetic^[18]. The magnetic behavior of complex **2** can be ascribed to the combination of possible magnetic interactions

and the depopulation of the Dy ions Stark levels. A strictly theoretical treatment of magnetic properties for this system is still a difficult task due to the large anisotropy of Dy(III) ion.

The field dependences of magnetizations for complex **2** is typical of a metamagnetic system with a sigmoidal curve. As show in Fig.5, the magnetization curve reveals two-step field induced transition. The first step is probably corresponds to the weak anti-ferromagnetic next-nearest-neighbor (NNN) interactions between chains. The spin flip transition at around 6 kOe, then as the magnetic field increases, M increases steadily to reach $8.41N\beta$ at 70 kOe. This step is probably nearest-neighbor (NN) ferromagnetic interactions between the Dy(III) and the radical.

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 frequency dependent out-of-phase signals indicating that it behaves as SCM.

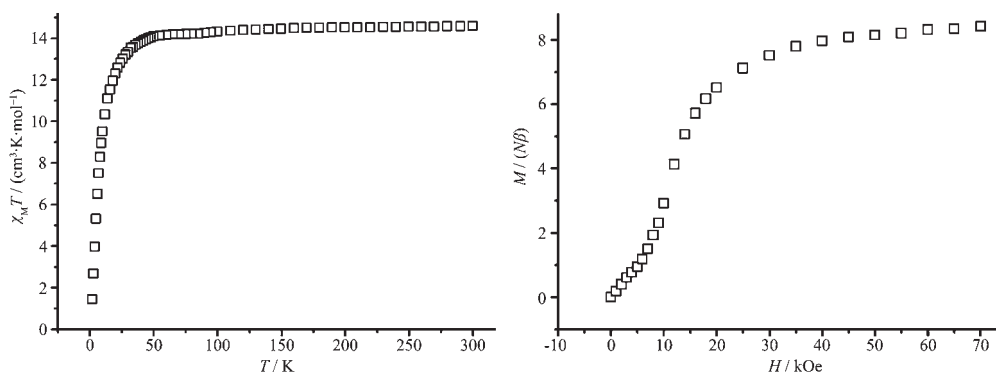


Fig.5 Temperature dependence of $\chi_M T$ for complex **2** (left) and field dependence of magnetization of **2** at 2.0 K (right)

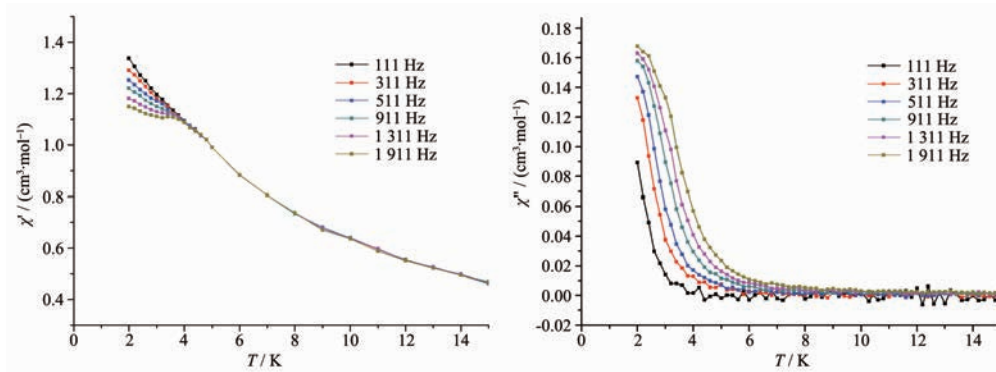


Fig.6 Temperature dependence of the in-phase (left) and out-of-phase (right) components of ac susceptibility for **2** in zero dc field with an oscillation of 3.5 Oe

3 Conclusions

In summary, two novel Dy(III)-radical complexes have been successfully obtained by choosing NIT-C₃H₅ as ligand and Dy(hfac)₃·2H₂O as salt with different synthetic conditions. Single crystal X-ray crystallographic analysis show that complex **1** is mononuclear complex while complex **2** is one-dimensional lanthanide-radical complex. Magnetic studies reveal that complex **2** exhibits frequency-dependence of ac magnetic susceptibilities indicating that it behaves as single-chain magnet.

Supporting information is available at <http://www.wjhxzb.cn>

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