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Syntheses, Crystal Structures, and Magnetic Properties of Two Monometallic Tri-Spin Complexes Involving Nitronyl Nitroxide Radicals-Lanthanide Ions[1]

R. N. Liu*, S. P. Zhao, and C. X. Xiong

School of Materials Science and Engineering, Wuhan Textile University, Wuhan, 430073 P.R. China

**e-mail: liuruina@mail.nankai.edu.cn*

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Abstract—Two new lanthanide-radical complexes $[Ln(Hfac)_3(NIT\text{-}4PhAllO)_2]$(Ln(III) = Gd (**I**), Tb (**II**); Hfac = hexafluoroacetylacetonate; NIT-4PhAllO = 4'-allyloxyphenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) have been prepared and characterized in structurally as well as magnetically. Single crystal X-ray diffraction analyses reveal that two complexes are isostructural with mononuclear tri-spin structure, in which the metal ions are eight-coordinated in distorted dodecahedron geometry. The nitronyl nitroxide radicals act as monodentate ligands towards $Ln(Hfac)_3$ unit through the oxygen atom of the nitronyl nitroxide group. Magnetic studies reveal that the Gd-coordinated nitroxide interaction is ferromagnetic.

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INTRODUCTION

The syntheses of molecular based magnetic materials by using nitronyl nitroxide radical-metal approach have attracted much interest in recent years [1–4]. First, nitronyl nitroxide radicals can act as not only spin carriers but also building blocks. Various organic radicals can be obtained through using different substituent groups. Second, most of the appealing results by using this method rely on coordination compounds of the first-row transition metal ions [5–9]. In contrast, metal-radical complexes based on rare-earth ions are less numerous [10–14]. The rather large and anisotropic magnetic moments of most of lanthanide(III) ions make such ions very appealing for the preparation of magnetic materials. The magnetic properties of lanthanide-nitronyl nitroxide (2*p*–4*f*) complexes are always attractive, some of them showing single molecular magnets and single chain magnets behavior [15–18]. In order to develop new molecular based magnetic materials involving nitroxide radicals-lanthanide ions, a new nitronyl nitroxide radical NIT-4PhAllO was prepared, and two new mononuclear tri-spin complexes $[Ln(Hfac)_3(NIT\text{-}4PhAllO)_2]$ (Ln = Gd (**I**), Tb (**II**)) were synthesized. Their magnetic properties were studied in this paper, showing that ferromagnetic interactions exist between lanthanide ions and coordinated N–O groups in complexes **I**, **II**.

EXPERIMENTAL

All chemicals and solvents used for the syntheses were reagent grade without further purification. The radical ligand NIT-4PhAllO was prepared according to literature method [19]. Elemental analyses for C, H, and N were obtained at the Institute of Elemental Organic Chemistry, Nankai University. Infrared spectra were taken on a Bruker Tensor 27 Fourier transform infrared spectroscopy in the 4000–400 cm^{-1} regions, using KBr pellets. Magnetic measurements were performed on a SQUID MPMS XL-7 magnetometer. Diamagnetic corrections were made with Pascal's constants for all of the constituent atoms.

Synthesis of I and II. The two complexes were synthesized following a procedure similar to that exemplified for **II** hereafter. A solution of $Tb(Hfac)_3 \cdot 2H_2O$ (0.0330 g, 0.04 mmol) in 20 mL of dry *n*-heptane was heated under reflux for 2 h. After that, the solution was cooled to about 80°C, and a solution of NIT-4PhAllO (0.012 g, 0.04 mmol) in 2 mL of CH_2Cl_2 was added. The resulting mixture was stirred for 1 h and then cooled to room temperature. After filtration, the resulting solution was left at room temperature for two days to give deep blue crystals suitable for X-ray analysis. The yields were: 68 (**I**) and 70% (**II**).

For $C_{47}H_{45}N_4O_{12}F_{18}Gd$ (**I**)

anal. calcd., %:	C, 41.60;	H, 3.34;	N, 4.13.
Found, %:	C, 41.70;	H, 3.24;	N, 4.17.

FT-IR (KBr; ν, cm^{-1}): 1656 ν(C=O), 1350 ν(N–O).

For $C_{47}H_{45}N_4O_{12}F_{18}Tb$ (**II**)

anal. calcd., %:	C, 41.54;	H, 3.34;	N, 4.12.
Found, %:	C, 41.62;	H, 3.24;	N, 4.08.

FT-IR (KBr; ν, cm^{-1}): 1655 ν(C=O), 1350 ν(N–O).

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Table 1. Crystallographic data and details of structure refinements for complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	1357.12	1358.79
Temperature	293(2) K	113(2) K
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	12.5115(7)	12.501(3)
b, Å	14.5462(8)	14.205(3)
c, Å	17.7380(10)	17.486(3)
α, deg	98.311(2)	98.30(3)
β, deg	105.761(2)	105.95(3)
γ, deg	109.728(2)	109.55(3)
Volume, Å^3	2823(3)	2716.1(10)
Z	2	2
ρ, mg/m^3	1.596	1.661
Absorption coefficient, mm^{-1}	1.294	1.426
Crystal size, mm	0.20 × 0.18 × 0.12	0.20 × 0.20 × 0.12
F(000)	1354	1356
θ Range, deg	3.00–27.49	1.84–25.02
Limiting indices h, k, l	$-16 \le h \le 16$, $-18 \le k \le 18$, $-23 \le l \le 23$	$-14 \le h \le 14$, $-16 \le k \le 16$, $-15 \le l \le 20$
Reflections collected/unique (R_{int})	28604/12846(0.0512)	17833/9525(0.0270)
Reflections with $I > 2\sigma(I)$	10599	8852
Data/restraints/parameters	12846/540/823	9525/144/803
Goodness-of-fit on F^2	1.077	1.046
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0535$, $wR_2 = 0.1074$	$R_1 = 0.0265$, $wR_2 = 0.0653$
R indices (all data)	$R_1 = 0.0714$, $wR_2 = 0.1157$	$R_1 = 0.0294$, $wR_2 = 0.0669$
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.970/–1.236	0.784/–0.919

X-ray structure determination. Single crystal of each compound for X-ray diffraction analyses with suitable dimensions was mounted on a glass fiber. Determination of the unit cell and data collection were performed with MoK_α radiation (λ = 0.71073 Å) on a Rigaku Saturn diffractometer equipped with a CCD camera. The ω–φ scan technique was employed. The structure was solved by direct methods and refined by full matrix least-squares on F^2 using SHELXS-97 and SHELXL-97 programs [20], respectively. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Details of the crystal parameters, data collection, and refinement of two compounds are summarized in Table 1. The important bond lengths and angles for complexes **I**, **II** are listed in Table 2.

Supplementary material for the structural analysis has been deposited with the Cambridge Crystallographic Data Center (nos. 845092 (**I**), 845091 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The molecular structures of two complexes are isostructural. The structure of complex **II** (Fig. 1) will be described as representation. In the asymmetric unit, there exist one crystallographically independent Tb(III) atom and two nitronyl nitroxide radicals to form mononuclear tri-spin structure. Tb(III) atom is eight-coordinated in which are occupied by six oxygen atoms from three didentate hfac ligands. The coordination spheres of the Tb(III) atom are completed by two oxygen atoms from two nitroxide groups. The coordination polyhedron may be represented as a distorted dodecahedron with triangular faces. NIT-4PhAllO radicals act as monodentate ligand towards Tb(III) atom through the oxygen atom of the nitronyl nitroxide group. The Tb–O(nitroxide) distances are 2.3636(18) and 2.3120(18) Å for Tb(1)–O(1) and Tb(1)–O(4), respectively, while the bond lengths of Tb–O(Hfac)

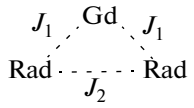
Table 2. Selected bond lengths and angles (deg) for complexes **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
	I		
Gd(1)–O(4)	2.330(3)	Gd(1)–O(11)	2.408(3)
Gd(1)–O(9)	2.350(3)	Gd(1)–O(10)	2.411(3)
Gd(1)–O(12)	2.361(3)	O(1)–N(1)	1.294(4)
Gd(1)–O(1)	2.370(3)	O(2)–N(2)	1.269(5)
Gd(1)–O(8)	2.377(3)	O(4)–N(3)	1.303(5)
Gd(1)–O(7)	2.380(3)	O(5)–N(4)	1.264(6)
	II		
Tb(1)–O(4)	2.312(18)	Tb(1)–O(11)	2.3868(18)
Tb(1)–O(9)	2.345(2)	Tb(1)–O(10)	2.3951(19)
Tb(1)–O(12)	2.347(2)	O(1)–N(1)	1.298(3)
Tb(1)–O(8)	2.3577(19)	O(2)–N(2)	1.273(3)
Tb(1)–O(1)	2.3636(17)	O(4)–N(3)	1.312(3)
Tb(1)–O(7)	2.367(2)	O(5)–N(4)	1.259(3)
Angle	ω, deg	Angle	ω, deg
	I		
O(1)Gd(1)O(4)	139.39(11)	N(1)O(1)Gd(1)	136.5(3)
N(3)O(4)Gd(1)	137.9(3)		
	II		
O(1)Tb(1)O(4)	139.00(6)	N(1)O(1)Tb(1)	134.56(15)
N(3)O(4)Tb(1)	134.97(16)		

are in the range of 2.3450(2)–2.3951(19) Å. These bond lengths are comparable to those of the reported $Ln(hfac)_3$ with nitronyl nitroxides [11–14, 21, 22]. Two coordinated nitroxide groups make angles of 139.0(6)° with Tb(III) atom for O(1)Tb(1)O(4). The dihedral angles between the phenyl rings and the ONCNO moieties are 27.2° and 26.1° for two independent NIT-4PhAllO radical ligands. Packing diagram of complex **II** is shown in Fig. 2. The shortest distance between Tb···Tb is 12.501 Å, and N–O···O–N is 9.238 Å.

The variable-temperature magnetic susceptibilities were measured using a SQUID magnetometer in the temperature range 2–300 K in an applied field of 2000 Oe for complexes **I**, **II**. The $\chi_M T$ and χ_M^{-1} vs. T plots for **I** are shown in Fig. 3a. At 300 K, the $\chi_M T$ value is 8.93 $cm^3 K mol^{-1}$, which is in good agreement with the expected value of 8.63 cm^3 K mol^{-1} for the isolated spins one $S_{Gd} = 7/2$ and two $S_{rad} = 1/2$. With a decrease in the temperature, the $\chi_M T$ value increases more and more rapidly to reach a maximum of 10.82 cm^3 K mol^{-1} at 2.0 K. These results are characteristic of a system with ferromagnetic interactions. During the all rang of the temperature, the magnetic susceptibilities obey the Curie–Weiss law, and the fitting results are Curie constant $C = 8.95$ cm^3 K mol^{-1}, Weiss constant $\theta = 2.49$ K, which also indicates that there exists ferromagnetic interactions in the system.

Based on structural analysis, there are mainly two kinds of magnetic interactions for the present magnetic system, namely: (i) the magnetic interaction between Gd ion and the directly coodinated nitroxide group (J_1); (ii) the magnetic coupling between two coordianted nitroxide groups through Gd(1) (J_2). Magnetic exchange pathways are shown below:



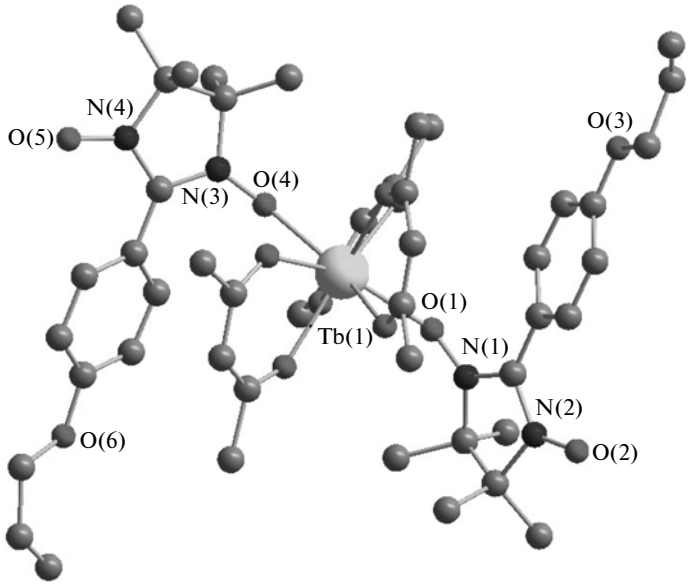


Fig. 1. Crystal structure of complex **II**. All hydrogen and fluorine atoms are omitted for clarity.

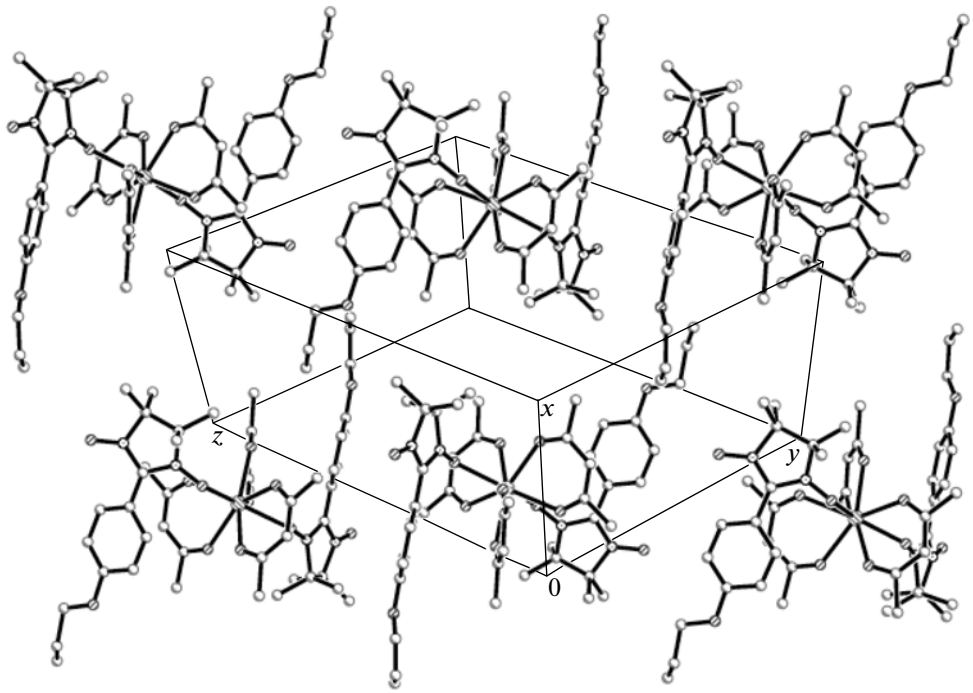


Fig. 2. Packing diagram of complex **II**.

The magnetic data were analyzed by a theoretical expression (1) deduced from the spin Hamiltonian $\boldsymbol{H} = -J_1(\boldsymbol{S}_{\mathrm{Rad1}}\boldsymbol{S}_{\mathrm{Gd1}} + \boldsymbol{S}_{\mathrm{Gd1}}\boldsymbol{S}_{\mathrm{Rad2}}) - J_2\boldsymbol{S}_{\mathrm{Rad1}}\boldsymbol{S}_{\mathrm{Rad2}}$.

$$\chi' = \frac{Ng^2\beta^2}{6kT}\frac{252\exp(9J_1/2kT - J_2/kT) + 495\exp(8J_1/kT) + 252\exp(7J_1/2kT) + 105}{8\exp(9J_1/2kT - J_2/kT) + 10\exp(8J_1/kT) + 8\exp(7J_1/kT) + 6}. \quad (1)$$

The best fitting leads to $g = 2.03$, $J_1 = 4.16$ cm^{-1}, $J_2 = -14.41$ cm^{-1}, $R = 7.76 \times 10^{-6}$ (R is defined as $\sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\sum[(\chi_M)_{obs}]^2$). These results indicate that the Gd-coordinated nitroxide interaction is ferromagnetic and the magnetic coupling between radicals through the Gd atom is antiferromagnetic, as already observed in such compounds [11, 14]. The ferromagnetic interaction between the Gd and radical can be understand as a consequence of electron transfer involving the magnetic orbital of the free radical (π^*) and the empty orbitals of the Gd(III) ion (5*d* or 6*s*) that stabilized the higher multiplicity ground spin state following Hund's rule [23, 24].

For compex **II**, the $\chi_M T$ and $\chi_M{}^{-1}$ versus T measurements (Fig. 3b) show a room temperature value of 12.64 cm^3 K mol^{-1}, close to 12.57 cm^3 K mol^{-1} expected for one uncorrelated Tb(III) (a $^7F_6$ ion) and two uncorrelated $S = 1/2$ spins. As temperature is lowered, the $\chi_M T$ value gradually decreases to reach a minimum of 12.10 cm^3 K mol^{-1} at 12 K, due to crystal-field effects on the Tb(III) Stark sub-level. Below 12 K, the $\chi_M T$ value increases rapidly to a maximum of 12.33 cm^3 K mol^{-1} at 9 K, then decreases to 11.45 cm^3 K mol^{-1} at 2 K. The profile of the curve indicates that the Tb(III)-coordinated nitroxide group interaction is ferromagnetic. The magnetic susceptibilities obey the Curie–Weiss law in the temperature range 2–300 K, and Curie constant $C = 12.68$ cm^3 K mol^{-1}, Weiss constant $\theta = -1.03$ K.

To examine the spin dynamics, the temperature dependence of the AC magnetic susceptibility was collected at zero dc field and an ac field of 3.5 Oe at frequencies of 100, 800, 1300 Hz. The temperature dependence of both in-phase (χ'_M) and out-of-phase signals (χ''_M) is depicted in Fig. 4, but the signals do not display frequency-dependence phenomenon. The result suggests that complex **II** is not a single molecular magnet (SMM).

In conclusion, we report two new radical-rare-earth complexes, which are mononuclear tri-spin structure-type. Magnetic studies show that the Gd-coordinated nitroxide interaction is ferromagnetic and the magnetic coupling between radicals through the Gd atom is antiferromagnetic in complexes **I**. For complex **II**, magnetic studies indicate that the Tb(III)-coordinated nitroxide group interaction is

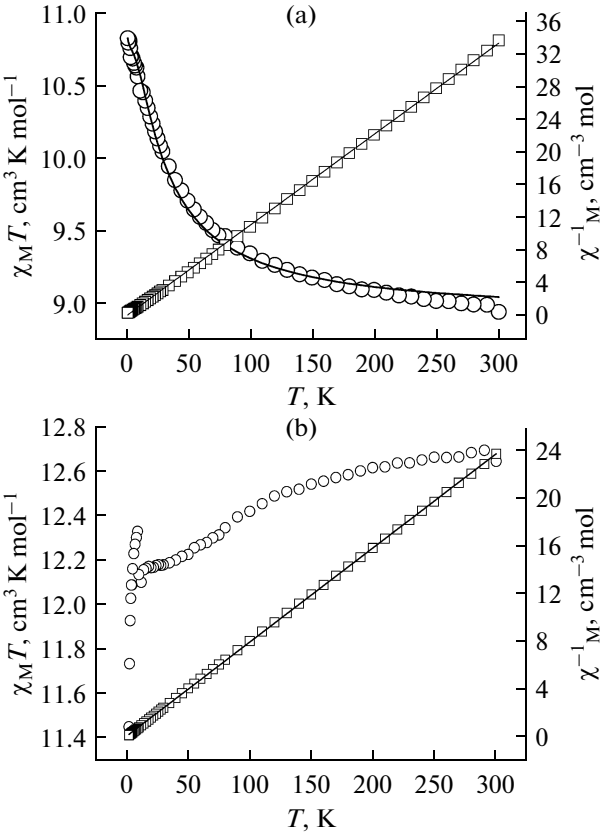


Fig. 3. Plots of $\chi_M T$(○) vs. T and χ^{-1} (□) vs. T for **I** (a) and **II** (b). The solid line represents the theoretical fit.

also ferromagnetic. These results provide an opening into a promising new field of molecular based magnetic materials based on the rare-earth ion and nitronyl nitroxide radical.

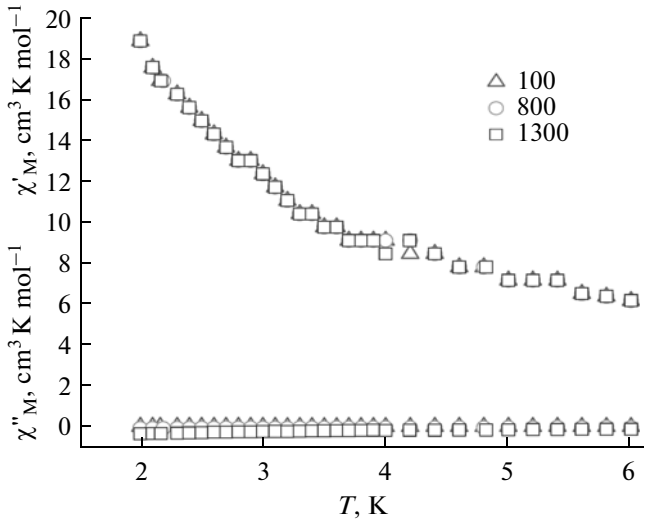


Fig. 4. Temperature dependence of in-phase and out-of-phase components of ac susceptibility for **II** in zero dc field with an oscillating of 3.5 Oe.

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