Two tri-spin complexes based on gadolinium and nitronyl nitroxide radicals: Structure and ferromagnetic interactions

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ABSTRACT

Three Radical–Ln(III)–Radical complexes based on nitronyl nitroxide radicals have been synthesized, structurally and magnetically characterized: [Gd(hfac)$_3$(NITPhOEt)$_2$] (**1**) (hfac=hexafluoroacetylacetonate, and NITPhOEt=4′-ethoxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide), [Gd(hfac)$_3$(NITPhOCH$_2$Ph)$_2$] (**2**) (NITPhOCH$_2$Ph=4′-benzyloxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) and [Lu(hfac)$_3$(NITPhOCH$_2$Ph)$_2$] (**3**). The X-ray crystal structure analyses show that the structures of the three compounds are similar and all consist of the isolated molecules, in which central ions Gd^{III} or Lu^{III} are coordinated by six oxygen atoms from three hfac and two oxygen atoms from nitronyl radicals. The magnetic studies show that in both of the two Gd^{III} complexes, there are ferromagnetic Gd^{III}–Rad interactions and antiferro-magnetic Rad–Rad interactions in the molecules (with J_{Rad-Gd}=0.27 cm^{-1}, $j_{Rad-Rad}$=−2.97 cm^{-1} for **1**: and J_{Rad-Gd}=0.62 cm^{-1}, $j_{Rad-Rad}$=−7.01 cm^{-1} for **2**). An analogous complex of [Lu(hfac)$_3$ (NITPhOCH$_2$Ph)$_2$] (**3**) containing diamagnetic Lu^{III} ions has also been introduced for further demonstrating the nature of magnetic coupling between radicals.

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1. Introduction

The design of new magnetic materials based on nitronyl nitroxide radicals is one of the most important research subjects for the chemistry and physics communities, until now the magnetic coupling between 2p–3d ions has been well understood [1–6], contrastively, molecular magnetic materials based on rare earth metal ions and nitronyl nitroxide radicals are less numerous, this may be attributed to the effective shielding by the outer-shell electrons and the rather large and anisotropic magnetic moments of the rare earth metal ions, which make their magnetic behaviours difficult to be treated [7–11]. However, that the gadolinium^{III} has f^7 electron configuration and quenched orbital angular momentum makes it easier to be studied, up to now many Gd^{III}–radical complexes have been obtained and their magnetic properties were studied in detail [11–19].

Previous experimental data have shown that most of Gd^{III}–radical complexes exhibit ferromagnetic coupling between the Gd^{III} and radicals, which was well explained as the result of electron transfer from the singly occupied π^* orbital of free radical into either the 5d or 6s of gadolinium^{III} [13–19]. However, some examples of antiferromagnetic couplings were recently reported such as semiquinonato radicals–Gd^{III} complexes [7,20], which may arise from a sensitive balance between two opposite

attributions, one from the direct overlap of the magnetic orbital of free radicals with the f orbitals, which presumably results in antiferromagnetic interactions, and the other from the overlap with 5d or 4s orbitals or the f orbitals are essentially orthogonal to the π^* orbitals which leads to ferromagnetism [7,20–22], and to acquire the independent information on these mechanisms, the isomorphous complexes were synthesized, where the nonmagnetic Y^{3+} ion replaces Gd^{3+}, which can provide information on the role of closed shells and empty orbitals [23].

Thus, there is an important point about the magnetic coupling between Gd^{III} and radicals, which must be still addressed. That is, why $J_{Rad-Gd} > 0$ in some cases, but $J_{Rad-Gd} < 0$ in others? Evidently, the design and characterization of new examples of various type of Gd^{III} and radicals complexes may aid to answer the question. With this aim, we herein report the synthesis, crystal structures and magnetic properties of two gadolinium^{III}–radicals complexes: [Gd(hfac)$_3$(NITPhOEt)$_2$] (**1**) and [Gd(hfac)$_3$(NITPhOCH$_2$Ph)$_2$] (**2**). To further demonstrate the nature of magnetic coupling between the intramolecular radicals, the [Lu(hfac)$_3$(NITPhOCH$_2$Ph)$_2$] (**3**) containing diamagnetic ions lutetium^{III} has also been synthesized and characterized.

2. Experimental

2.1. Materials

All of the reagents used in the syntheses were of analytical grade, the hexafluoroacetylacetone , the 4-(ethoxy)benzaldehyde

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and 4-(benzyloxy)benzaldehyde were purchased from Alfa Chemical Company, and the starting radicals [24] and Gd(hfac)$_3$···2H$_2$O [25,26] were synthesized according to the literature methods.

2.2. Syntheses of [Gd(hfac)$_3$(NITPhOEt)$_2$] (**1**), [Gd(hfac)$_3$(NITPhOCH$_2$Ph)$_2$] (**2**) and [Lu(hfac)$_3$(NITPhOCH$_2$Ph)$_2$] (**3**)

All of the three complexes were synthesized by the same method. Therefore, the synthesis of compound **1** is detailed herein. Gd(hfac)$_3$···2H$_2$O (0.1 mmol) was dissolved in boiling dry *n*-heptane (20 mL). After stirring for 1 h, the solution was cooled to 60 °C, to which NITPhOEt (0.1 mmol) in CH$_2$Cl$_2$ (5 mL) was added with stirring for 30 min. Then the solution was cooled to room temperature, filtrated and the filtrate was stored in a refrigerator at 4 °C for several days to give blue-violet crystals, which are suitable for X-ray analysis [27]. The compound of **2** was obtained in the similar manner using NITPhOCH$_2$Ph radical instead of NITPhOEt radical and the compound of **3** was obtained also in the similar manner using NITPhOCH$_2$Ph and Lu(hfac)$_3$···2H$_2$O instead of the corresponding reagents.

For complex **1**, yield [Gd(hfac)$_3$(NITPhOEt)$_2$] (0.03 g, 45%) Analysis: C$_{45}$H$_{45}$GdF$_{18}$N$_4$O$_{12}$: calcd: C 40.54, H 3.40, N 4.20; found: C 40.51, H 3.38, N 4.21% (carried out on a Perkin-Elmer elemental analyzer model 240). IR spectra of complex **1** (KBr cm^{-1}): 1654(vs), 1608(w), 1557(w), 1396(w), 1376(w), 1256(vs), 1201(vs), 1097(w).

For complex **2**, yield [Gd(hfac)$_3$(NITPhOCH$_2$Ph)$_2$] (0.04 g, 55%) Analysis: C$_{55}$H$_{49}$GdF$_{18}$N$_4$O$_{12}$: calcd: C 45.33, H 3.39, N 3.85; found: C 45.35, H 3.42, N 3.89%. IR spectra of complex **2** (KBr cm^{-1}): 1655(vs), 1605(w), 1556(w), 1397(w), 1376(w), 1256(vs), 1208(vs), 1097(w).

For complex **3**, yield [Lu(hfac)$_3$(NITPhOCH$_2$Ph)$_2$](0.05 g, 68%) Analysis: C$_{55}$H$_{49}$LuF$_{18}$N$_4$O$_{12}$: calcd: C 44.79, H 3.35, N 3.80; found: C 44.76, H 3.34, N 3.79%. IR spectra of complex **3** (KBr cm^{-1}): 1658(vs), 1606(w), 1556(w), 1397(w), 1376(w), 1256(vs), 1208(vs), 1101(w) [27].

2.3. X-ray structure determinations

Crystal systems, accurate cell constants, space group, and intensity data for complexes **1** and **2** were obtained in the room temperature from single crystals mounted on an Rigaku Saturn diffractometer using with Mo*K*α radiation (λ=0.71073 Å). The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL 97 software. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the final refinement model in calculated positions with isotropic thermal parameters [28,29].

2.4. Magnetic measurement

All the magnetic studies were performed on a crushed polycrystalline sample in order to avoid the anisotropy of these materials. The temperature dependence of the magnetic susceptibilities for the gadolinium complexes was measured on a SQUID magnetometer MPMS-7 in the range of 1.8–300 K. Measurements of the magnetic field dependence of the magnetization were performed on the same magnetometer at 1.9 K and in the field range of 0–70 kOe. The data were corrected for diamagnetic with Pascal's constants.

3. Results and discussion

3.1. Description of the crystal structure

The X-ray crystal structure analyses showed that complexes **1**, **2** and **3** have the similar structure and the crystallographic data are shown in Table 1. All the complexes consist of isolated molecules where the nitronyl nitroxide radicals act as monodentate ligands towards Gd^{III} or Lu^{III} through the oxygen atom of N–O group to form the monometallic Radical–Ln(III)–Radical complexes. The structure of complex **2** shown in Fig. 1(b) is an asymmetric isolated molecule [Gd(hfac)$_3$(NITPhOCH$_2$Ph)$_2$],

Table 1
Crystallographic data for complexes **1**, **2** and **3**.

	Complex **1**	Complex **2**	Complex **3**
Empirical formula	C$_{45}$H$_{45}$F$_{18}$GdN$_4$O$_{12}$	C$_{55}$H$_{49}$F$_{18}$GdN$_4$O$_{12}$	C$_{55}$H$_{49}$F$_{18}$LuN$_4$O$_{12}$
Formula weight	1333.10	1457.23	1474.95
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.293(3)	12.247(2)	12.363(3)
b (Å)	14.315(3)	15.908(3)	15.987(3)
c (Å)	17.624(3)	17.430(3)	17.562(4)
α (deg)	98.04(3)	72.38(3)	72.18(3)
β (deg)	103.78(3)	73.68(3)	73.08(3)
γ (deg)	111.71(3)	77.39(3)	77.48(3)
Volume (Å^3)	2707.7(10)	3072.9(9)	3130.3(11)
Z	2	2	2
ρ_{calc} (g cm^{-3})	1.642	1.575	1.690
μ (mm^{-1})	1.347	1.195	1.195
F(000)	1334	1458	1472
Reflections collected	27452	25971	30965
Unique/parameters	12361/843	10854/807	14072/819
R(int)	0.0462	0.0263	0.0517
Completeness to theta=27.48	99.4%	99.7%	99.7%
Max./min. transmission	0.8403/0.7532	0.866/0.751	0.8229/0.6489
Goodness-of-fit on F^2	1.058	1.072	1.069
Final R indices [$I > 2\mathrm{sigma}(I)$]	$R1$=0.0476, w$R2$=0.1011	$R1$=0.0328, w$R2$=0.0787	$R1$=0.0472, w$R2$=0.1067
R indices (all data)	$R1$=0.0629, w$R2$=0.1074	$R1$=0.0375, w$R2$=0.0816	$R1$=0.0605, w$R2$=0.1159

in which the central Gd^{III} ions are coordinated by six oxygen atoms from three hfac and two oxygen atoms from nitronyl nitroxide radicals. The coordination polyhedron of Gd^{III} can be best described as a distorted dodecahedron with triangular faces [12,30,31]. The Gd–O$_{Rad}$ bond lengths are 2.3216(17) and 2.3616(17) Å, while the Gd–O distances with hfac are in the range of 2.3464(16)–2.3959(17) Å. The shortest distance between Gd–Gd is 10.719 Å, the nearest distance of the uncoordinated N–O group is 3.154 Å, and the angle of O$_{Rad}$–Gd^{III}–O$_{Rad}$ is 139.15(6)°.
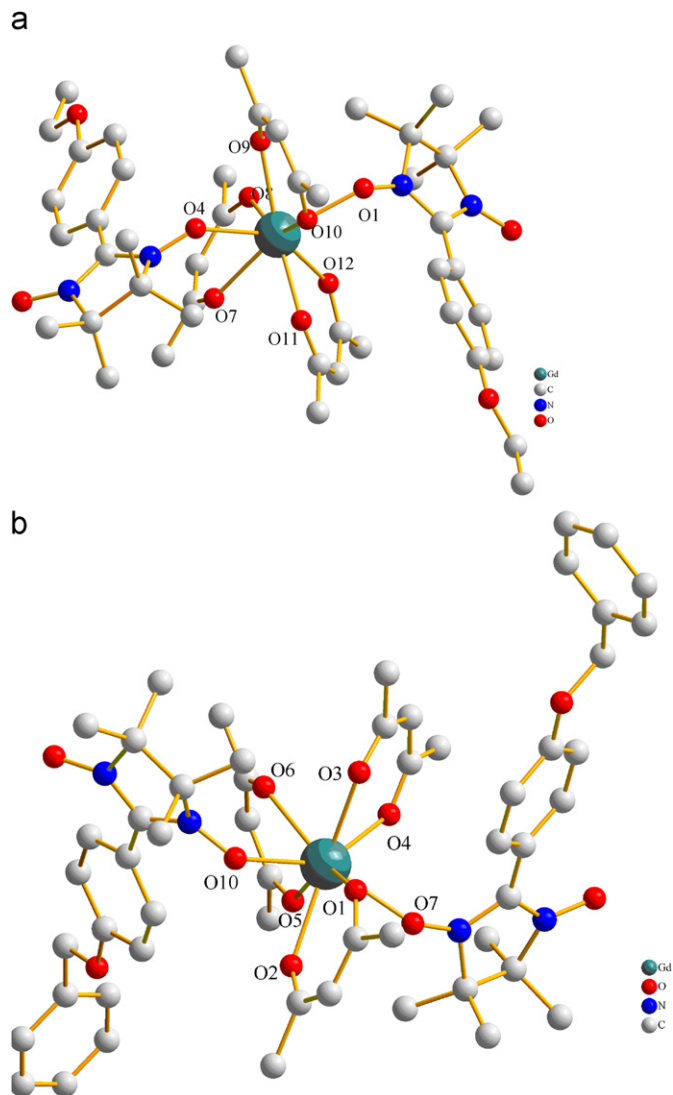

Fig. 1. (a) View of the [Gd(hfac)$_3$(NITPhOEt)$_2$] (**1**); (b) View of the [Gd(hfac)$_3$ (NITPhOCH$_2$Ph)$_2$] (**2**). The H and F atoms were omitted for clarity.

While for complex **3**, [Lu(hfac)$_3$(NITPhOCH$_2$Ph)$_2$] is isomorphic to complex **2** except for the substitution of Gd^{III} with the diamagnetic Lu^{III} ion, and the structure of complex **1** is also very similar to complex **2** except for the difference in the radicals, which makes the bond distances and angles vary a little. For complex **1**, the shortest distance between Gd–Gd is 10.125 Å, the nearest distance of the uncoordinated N–O group is 4.244 Å, and the angle of O$_{Rad}$–Gd^{III}–O$_{Rad}$ is 139.68(7)°. The selected bond lengths and angles for complexes **1**–**3** are all shown in Table 2, and the detailed structural information is also shown in Tables 1–3 in the supporting information.

3.2. UV absorption spectra

The UV absorption spectra for both of the two Gd^{III} complexes were measured using methanol as solvent. Absorption spectra of [Gd(hfac)$_3$(NITPhOEt)$_2$] (**1**) and [Gd(hfac)$_3$ (NITPhOCH$_2$Ph)$_2$] (**2**) are compared with the absorption spectra of NITPhOEt and NITPhOCH$_2$Ph, respectively (The figures are shown in the supporting information). Both of the two complexes have the similar absorption bands, 27.5×10^3 cm^{-1} are assigned to the π–π^* transitions of the conjugated ONCNO in the nitronyl nitroxide radicals [32,33], in view of the similarity in position with the UV absorption spectra of nitronyl nitroxide radicals. The higher frequency absorption bands for both of the two complexes around 33.9×10^3 cm^{-1} were assigned to the π–π^* transition or the charge transfer originating from other parts of the ligands like phenyl [7,32,33].

3.3. Magnetic properties

The temperature dependence of the magnetic susceptibilities for complexes **1** and **2** has the similar trend as shown in Fig. 2 and 3. The $\chi_M T$ value at room temperature is 8.84 and 8.79 cm^3 K mol^{-1} for complexes **1** and **2**, respectively, corresponding to the value (8.63 cm^3 K mol^{-1}) expected for an uncoupled system for one Gd^{III} ions ($S=7/2$) and two organic radicals ($S=1/2$) [12,27,34]. Upon cooling, for complex **1**, the $\chi_M T$ keeps almost constant until 50 K, and then increases steadily to a maximum of 9.86 cm^3 K mol^{-1} at 7 K, afterward decreases to 9.21 cm^3 K mol^{-1} at 2.0 K. While for **2**, the $\chi_M T$ keeps almost constant until 100 K, and then increases steadily to a maximum of 9.61 cm^3 K mol^{-1} at 14 K, afterward decreases to 9.21 cm^3 K mol^{-1} at 2.0 K. For both of the two complexes **1** and **2**, the increasing trends of $\chi_M T$ value upon cooling indicate the existence of ferromagnetic interactions in the molecule, and the decrease of the $\chi_M T$ below 7 K for complex **1** and 14 K for complex **2** may be due to the intermolecular antiferromagnetic interactions and the near distance of the uncoordinated N–O groups may be the origin of the intermolecular antiferromagnetic interactions [28,29].

As shown in Scheme 1, there are two kinds of interactions coexistence in the tri-spin complexes, Gd(III)–radical and radical–radical interactions. To evaluate the exchange coupling
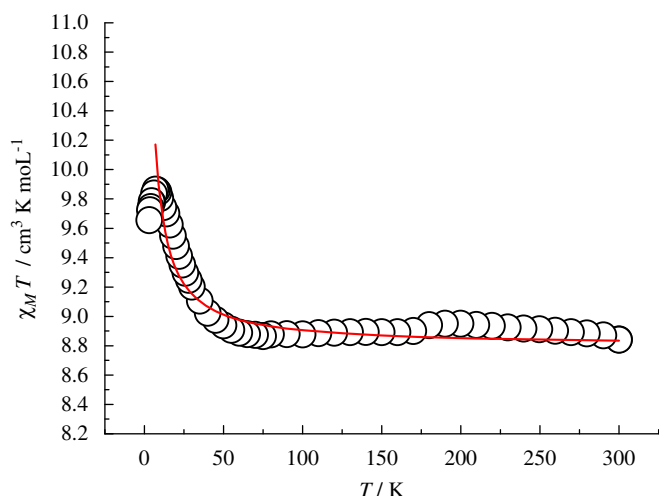
Table 2

The important interatomic distances [Å] and angles [deg] for complexes **1, 2** and **3**.

Complex	**1**(Ln=Gd)	**2**(Ln=Gd)	**3**(Ln=Lu)
Ln–O$_{Rad}$ length (Å)	2.316(2) and 2.363(2)	2.3216(17) and 2.3616(17)	2.265(2) and 2.325(2)
Ln–O$_{hfac}$ length (Å)	2.333(2)–2.391(2)	2.3464(16)–2.3959(17)	2.2918(19)–2.346(2)
Coordinated N–O$_{Rad}$ length (Å)	1.291(3) and 1.299(3)	1.300(3) and 1.296(3)	1.322(3) and 1.302(3)
Uncoordinated N–O$_{Rad}$ length (Å)	1.246(4) and 1.258(4)	1.252(3) and 1.269(3)	1.261(4) and 1.286(4)
Angle of O$_{Rad}$–Ln–O$_{Rad}$ (deg)	139.68(7)	139.15(6)	138.45(7)

O$_{Rad}$: the oxygen atoms of nitronyl nitroxide radicals; O$_{hfac}$: the oxygen atoms from hfac.

Fig. 2. Experimental (○) and calculated (—) $\chi_M T$ vs. T curve for compound of **1** [Gd(hfac)$_3$(NITPhOEt)$_2$] in the range of 1.8–300 K in the field of 1000 Oe and the experimental values are not fitted below 7 K.
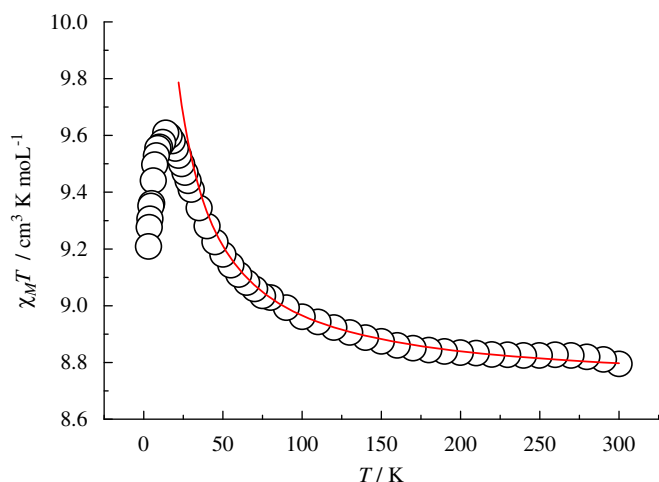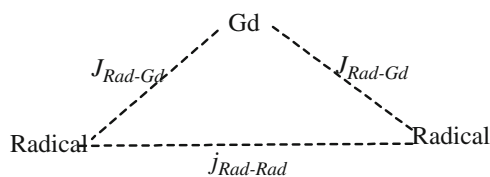

Fig. 3. Experimental (○) and calculated (—) $\chi_M T$ vs. T curve for compound of **2** [Gd(hfac)$_3$(NITPhOCH$_2$Ph)$_2$] in the range of 1.8–300 K in the field of 1000 Oe and the experimental values are not fitted below 14 K.

Scheme 1. The model of intramolecular interactions.

constants in such a magnetic system, considering Gd^{III} with an $^8S_{7/2}$ ground state, the magnetic interactions between Gd^{III} and the radicals can be well described by isotropic exchange interaction. Therefore, the experimental data for complexes **1** and **2** were analyzed with an expression derived from a spin Hamiltonian (Eq. (1)) [12,27,29], considering the Gd(III)–radical interactions J_{Rad-Gd}, and radical–radical interaction $j_{Rad-Rad}$ (shown in Scheme 1), assuming that radical and Gd^{III} have the same g value [25].

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

$$\chi_M = \frac{Ng^2\beta^2}{4kT}\left[\frac{A}{B}\right]$$

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

$$B = 5 + 4\exp\left(-\frac{9J_{Rad-Gd}}{kT}\right) + 4\exp\left(-\frac{7J_{Rad-Gd}+2j_{Rad-Rad}}{kT}\right)$$
$$+ 3\exp\left(-\frac{16J_{Rad-Gd}}{kT}\right) \tag{1}$$

Moreover, it must be remembered that $j_{Rad-Rad}$ in symmetric trinuclear species is usually obtained with rather poor accuracy from magnetic data of trinuclear species due to the large covariance [14,15]. Thus, we analyzed the interactions between the intramolecular radicals firstly by analyzing the complex of **3** [Lu(hfac)$_3$(NITPhOCH$_2$Ph)$_2$], which is structurally identical to complex **2**, except for the substitution of Gd^{III} with the diamagnetic Lu^{III} center [11,27]. The temperature dependence of the susceptibility for [Lu(hfac)$_3$(NITPhOCH$_2$Ph)$_2$] (**3**) χ_M vs. T and $\chi_M T$ vs. T has been studied, the experimental $\chi_M T$ value at room temperature is 0.749 cm^3 K mol^{-1} (Fig. 4), which corresponds well with two uncoupled nitronyl nitroxide radicals value (0.75 cm^3 K mol^{-1}). Upon cooling, the $\chi_M T$ value decreases slowly until 45 K, it decreases rapidly to 0.15 cm^3 K mol^{-1}. The above behaviour suggested the antiferromagnetic interaction between the intramolecular radicals. Because the Lu^{III} ion is diamagnetic, the magnetic susceptibility expression derived from a spin Hamiltonian $H = -2j_{Rad-Rad}\hat{S}_{Rad1}\hat{S}_{Rad2}$ was applied to the $\chi_M T$ vs. T plots in the range of 4.2–300 K, with a fixed g value at 2.0 [35], getting the results: $j_{Rad-Rad} = -7.72$ cm^{-1}, with $R = 4.87 \times 10^{-3}$, $(R = \sum(\chi T_{obs} - \chi T_{calc})^2 / \sum(\chi T_{obs})^2)$. The negative value of the $j_{Rad-Rad}$ demonstrates that in this kind of Radical–Ln^{III}–Radical system, the interactions between the intramolecular radicals are antiferromagnetic [11,27].

Considering the antiferromagnetic intramolecular radical interactions in Rad–Lu^{III}–Rad complex **3**, we assumed that the radical interactions in complex **2** were also antiferromagnetic, because of their isomorphic structure with the same radical. The best fit of the experimental data in the range of 14–300 K (Fig. 3) of **2** was obtained (we did not analyze the data under low temperature area, because
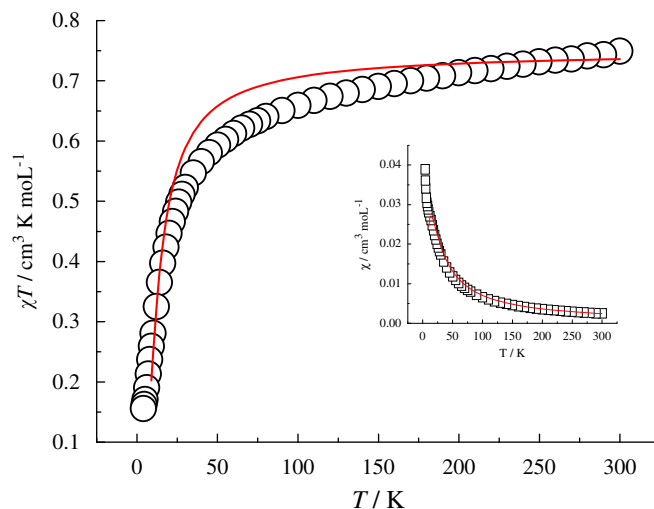

Fig. 4. Experimental (○) and calculated (—) $\chi_M T$ vs. T curve for compound of **3** [Lu(hfac)$_3$(NITPhOCH$_2$Ph)$_2$] in the range of 4.2–300 K in the field of 2000 Oe. Inset: χ_M vs. T plot for compound of **3**.

the effect of the intermolecular interaction becomes significant): $g=2.01$, $J_{Rad-Gd}=0.62$ cm^{-1}, $j_{Rad-Rad}=-7.01$ cm^{-1} [11,12,27], and the agreement factor $R=2.30\times10^{-4}$, ($R=\sum(\chi T_{obs}-\chi T_{calc})^2/\sum(\chi T_{obs})^2$). The positive value of J_{Rad-Gd} indicates the weak ferromagnetic interaction between the Gd^{III} and the radicals, the negative $j_{Rad-Rad}$ proved again the antiferromagnetic interaction between the two intramolecular radicals [5,11,12,27], which corresponds to the complex of **3**.

And for complex of **1**, the same model was applied to the $\chi_M T$ vs. T plots in the range of 7–300 K (Fig. 2) giving $g=2.02$, $J_{Rad-Gd}=0.27$ cm^{-1}, $j_{Rad-Rad}=-2.97$ cm^{-1}, with $R=9.27\times10^{-5}$ ($R=\sum(\chi T_{obs}-\chi T_{calc})^2/\sum(\chi T_{obs})^2$). And the positive value of J_{Rad-Gd} also indicates the weak ferromagnetic interaction between the Gd^{III} and the radicals, the negative $j_{Rad-Rad}$ proves the antiferromagnetic interaction between the two intramolecular radicals [11,12,27–29]. It is not clear why the $j_{Rad-Rad}$ value between radical–radical for complexes **2** and **3** differs so much. For complexes **1** and **2** this antiferromagnetic interaction between radicals can be transmitted by two different pathways, namely (1) exchange interaction through metal center Gd(III); (2) magnetic dipole–dipole interaction through space. The much larger $j_{Rad-Rad}$ for complex **2** than **1** may be due to the fact that complex **2** is more efficient in propagating antiferromagnetic exchange interaction through metal center because of the presence of the conjugated group (phenyl). Further studies with other complexes of this kind should be made to settle this point [36].

Either for complex **1** or complex **2**, the fitting results are all in the range of ever reported Gd^{III}–radicals compounds (Table 3). According to the literatures, some experts considered that the magnitude of the J_{Rad-Gd} was related to the angle of the O–Gd^{III}–O [37], in which the oxygen atoms are from the radicals; and some experts believed that the magnitude was related to the O–Gd^{III} distance between radical and Gd^{III} [38], others believed that was related to the angle of the Gd–O–N [11]. But by carefully comparing the structure of complexes **1**, **2** and the similar complexes reported in the literatures (Table 4), the

corresponding distances and angles are found to be similar, so no clear trend is observed relating the Gd^{III}–radical magnetic interaction to the molecular structure [38].

The field dependence of the magnetization of complexes **1** and **2** was measured at 1.90 K in the range of 0–70 kOe, the M vs. H curves are shown in Fig. 5(a) and (b). In both the figures, the experimental magnetization is compared to the theoretical magnetization given by the Brillouin function for $S=9/2$ of the ferromagnetic state and the $S=7/2$ for antiferromagnetic state. The experimental magnetization is lower than that expected for $S=9/2$ state, but higher than $S=7/2$ state, which may be due to the coexistence of ferromagnetic interactions and antiferromagnetic interactions [40,41] and the spin frustration of Gd^{III} under the influence of the contrasting interaction between the intramolecular radicals [42].

The ferromagnetic interaction between Gd^{III} and radicals can be interpreted by a mechanism suggested by D. Gatteschi and P. Rey [12,13]: on the basis of a simple angular overlap analysis, the π^* orbitals of one radical can interact with a linear combination of f orbitals $(4z^2-x^2-y^2)x$ and $(3x^2y-y^3)$ and that of the other radical interacts with $(4z^2-x^2-y^2)y$ and (x^3-3xy^2), which yield a weak antiferromagnetic interaction, while the other combinations of f orbitals are essentially orthogonal to the π^* orbitals and may give ferromagnetic contributions. The experimental data for complexes of **1** and **2** indicate that the latter dominates.

4. Summary and conclusions

In this paper, two mononuclear tri-spin compounds based on Gd^{III}–radical have been synthesized and characterized, and the ferromagnetic interactions between Gd–Radical and antiferromagnetic interactions between the intramolecular radicals coexist in these systems. The weak magnetic interactions show that though the f orbits of Gd^{III} are relatively shielded, they can nevertheless interact with the orbitals of the radical, thus giving

Table 3
The magnetic interactions in the compounds reported in the literatures.

	Compound	J_{Rad-Gd} (cm^{-1})	$j_{Rad-Rad}$ (cm^{-1})	Ref.
1	[Gd(NITtrz)$_2$(NO$_3$)$_3$]	+3.0	−3.5	[37,38]
2	[Gd(NITMeBzImH)$_4$] ⋯(ClO$_4$)$_3$⋯2THF	−3.8	−5.6	[39]
3	[Gd(NITBzImH)$_4$](ClO$_4$)$_3$	−1.8	−7.2	[39]
4	[Gd(NITBzImH)$_2$(NO$_3$)$_3$]	−4.05, −0.80	−1.1	[7]
5	[Gd(hfac)$_3$(NITEt)$_2$]	+0.25	−2.1	[11]
6	[Gd(hfac)$_3$(NITPh)$_2$]	+1.022	−1.65	[12]
7	[Gd(hfac)$_3$(NITPh)$_2$]	+0.61	−2.6	[11]
8	[Gd(hfac)$_3$(NITPh-p-Cl)$_2$]	+0.62	–	[34]
9	[Gd(hfac)$_3$(NITPhOMe)$_2$]	+1.48	−1.82	[27]
10	[Gd(hfac)$_3$(NITPhOEt)$_2$]	+0.27	−2.97	This work
11	[Gd(hfac)$_3$(NITPhOCH$_2$Ph)$_2$]	+0.62	−7.01	This work

To compare, the values of J in the literature have been converted based on the same standard of J symbol.

Table 4
The magnetic interactions and the correlative distances and angles of the compounds reported in the literatures.

| Compound	Angle of O$_{Rad}$–Gd^{III}–O$_{Rad}$ (deg)	Length of O$_{Rad}$–Gd^{III} (Å)	Angle of Gd^{III}–O$_{Rad}$–N$_{Rad}$ (deg)	J_{Rad-Gd} (cm^{-1})	$j_{Rad-Rad}$ (cm^{-1})	Ref.
[Gd(hfac)$_3$(NITPh)$_2$]	138.14	2.324 and 2.338	141.61 and 144.64	+1.022	−1.65	[12]
[Gd(hfac)$_3$(NITPh)$_2$]	Not found	2.327(5) and 2.337(5)	141.1 and 144.6	+0.61	−2.6	[11]
[Gd(hfac)$_3$(NITPh-p-Cl)$_2$]	137.78	2.354 and 2.345	141.67 and 143.24	+0.62	–	[34]
[Gd(hfac)$_3$(NITPhOMe)$_2$]	137.6(2)	2.348(5)	140.94 and 141.10	+1.48	−1.82	[27]
[Gd(hfac)$_3$(NITPhOEt)$_2$]	139.68(7)	2.316(2) and 2.363(2)	138.63(18) and 135.77(17)	+0.27	−2.97	This work
[Gd(hfac)$_3$(NITPhOCH$_2$Ph)$_2$]	139.15(6)	2.3216(17) and 2.3616(17)	138.5(2) and 137.8(3)	+0.62	−7.01	This work

a

b
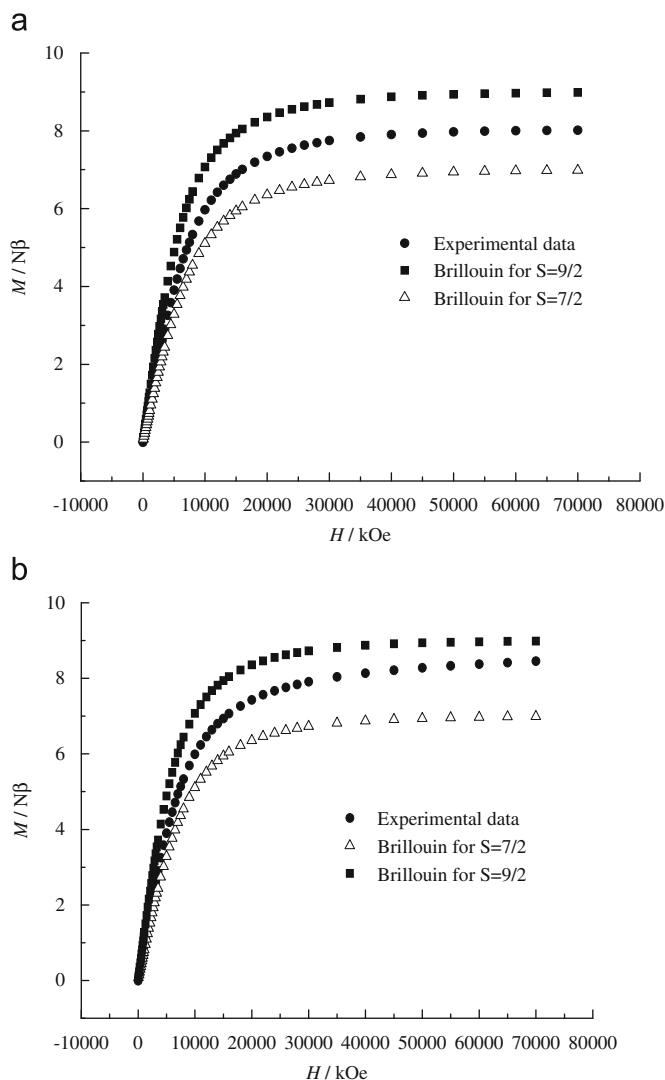
Fig. 5. Field dependence of the magnetization plots: (a) for complex **1** and (b) for **2** at 1.90 K. Compared with the Brillouin function for antiferromagnetic $S=7/2$ ($\triangle$) and the Brillouin for ferromagnetic $S=9/2$($\blacksquare$) state.

rise to appreciable coupling [11,27,41]. And the introduction of the diamagnetic Lu^{III} to this system can also demonstrate the antiferromagnetic interactions between the radicals, but the magnitude of the $J_{Rad–Gd}$ trend is not clear at all, much work should be done to make further study.

Supporting information

The structural information about complex **3**, IR spectra, UV spectra. CCDC number 728225 for complex of **1**, 728590 for complex of **2** and 734832 for complex of **3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.02.012.

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