



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(NITPhOCH₂Ph)₂] (**2**) (NITPhOCH₂Ph = 4'-benzyloxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) and [Lu(hfac)₃(NITPhOCH₂Ph)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 $J_{Rad-Gd} = 0.27 \text{ cm}^{-1}$, $J_{Rad-Rad} = -2.97 \text{ cm}^{-1}$ for **1**; and $J_{Rad-Gd} = 0.62 \text{ cm}^{-1}$, $J_{Rad-Rad} = -7.01 \text{ cm}^{-1}$ for **2**). An analogous complex of [Lu(hfac)₃(NITPhOCH₂Ph)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 Y³⁺ ion replaces Gd³⁺, 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(NITPhOCH₂Ph)₂] (**2**). To further demonstrate the nature of magnetic coupling between the intramolecular radicals, the [Lu(hfac)₃(NITPhOCH₂Ph)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 $\text{Gd}(\text{hfac})_3 \cdots 2\text{H}_2\text{O}$ [25,26] were synthesized according to the literature methods.

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

All of the three complexes were synthesized by the same method. Therefore, the synthesis of compound **1** is detailed herein. $\text{Gd}(\text{hfac})_3 \cdots 2\text{H}_2\text{O}$ (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_2Cl_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 NITPhOCH₂Ph radical instead of NITPhOEt radical and the compound of **3** was obtained also in the similar manner using NITPhOCH₂Ph and $\text{Lu}(\text{hfac})_3 \cdots 2\text{H}_2\text{O}$ instead of the corresponding reagents.

For complex **1**, yield $[\text{Gd}(\text{hfac})_3(\text{NITPhOEt})_2]$ (0.03 g, 45%) Analysis: $\text{C}_{45}\text{H}_{45}\text{GdF}_{18}\text{N}_4\text{O}_{12}$; 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 $[\text{Gd}(\text{hfac})_3(\text{NITPhOCH}_2\text{Ph})_2]$ (0.04 g, 55%) Analysis: $\text{C}_{55}\text{H}_{49}\text{GdF}_{18}\text{N}_4\text{O}_{12}$; 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 $[\text{Lu}(\text{hfac})_3(\text{NITPhOCH}_2\text{Ph})_2]$ (0.05 g, 68%) Analysis: $\text{C}_{55}\text{H}_{49}\text{LuF}_{18}\text{N}_4\text{O}_{12}$; 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 $\text{MoK}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$). 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 $[\text{Gd}(\text{hfac})_3(\text{NITPhOCH}_2\text{Ph})_2]$,

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

	Complex 1	Complex 2	Complex 3
Empirical formula	$\text{C}_{45}\text{H}_{45}\text{F}_{18}\text{GdN}_4\text{O}_{12}$	$\text{C}_{55}\text{H}_{49}\text{F}_{18}\text{GdN}_4\text{O}_{12}$	$\text{C}_{55}\text{H}_{49}\text{F}_{18}\text{LuN}_4\text{O}_{12}$
Formula weight	1333.10	1457.23	1474.95
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	12.293(3)	12.247(2)	12.363(3)
<i>b</i> (Å)	14.315(3)	15.908(3)	15.987(3)
<i>c</i> (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)
<i>Z</i>	2	2	2
ρ_{calc} (g cm ⁻³)	1.642	1.575	1.690
μ (mm ⁻¹)	1.347	1.195	1.195
<i>F</i> (000)	1334	1458	1472
Reflections collected	27452	25971	30965
Unique/parameters	12361/843	10854/807	14072/819
<i>R</i> (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 <i>R</i> indices [$I > 2\sigma(I)$]	<i>R</i> 1=0.0476, <i>wR</i> 2=0.1011	<i>R</i> 1=0.0328, <i>wR</i> 2=0.0787	<i>R</i> 1=0.0472, <i>wR</i> 2=0.1067
<i>R</i> indices (all data)	<i>R</i> 1=0.0629, <i>wR</i> 2=0.1074	<i>R</i> 1=0.0375, <i>wR</i> 2=0.0816	<i>R</i> 1=0.0605, <i>wR</i> 2=0.1159

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