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Syntheses, crystal structures, magnetic properties of two new lanthanide-nitronyl nitroxide complexes ($Ln^{III} = Gd^{III}, Nd^{III}$)

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ABSTRACT

Two new complexes based on lanthanide ions and nitronyl nitroxide radical, $Ln(hfac)_3(NITPh\text{-}p\text{-}Cl)_2$ (Ln = Gd(**1**), Nd(**2**); hfac = hexafluoroacetylacetonate; NITPh-p-Cl = 2-(4′-chlorphenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) have been synthesized and characterized by single-crystal X-ray diffraction. The single-crystal structures show that two complexes have similar structures, which consist of radical–Ln–radical isolated molecules. The Ln(III) ions are eight-coordinated in slightly distorted dodecahedral geometry. NITPh-p-Cl molecules act as monodentate ligands linking two Ln(III) ions through the oxygen atoms of the N–O groups. The magnetic studies show that the spin coupling between the Gd(III) ion and the radicals in the complex **1** is weak ferromagnetic ($J = 0.38\ cm^{-1}$), while complex **2** exhibits antiferromagnetic interactions ($zJ' = -0.36\ cm^{-1}$) between Nd(III) ion and radicals.

1. Introduction

In the filed of molecule-based magnetic materials, metal complexes with nitronyl nitroxide ligands have attracted much attention in recent years [1,2], especially for the systems containing lanthanide metal ions [3,4]. Indeed, Lanthanide ions become good candidates for the construction of molecular-based magnetic materials due to their large number of unpaired f-electrons and large intrinsic magnetic anisotropy [5], furthermore, exhibit unique topological structure leading to luminescence and magnetic properties when coordinated with geometry suitable ligands [6–8]. Nitronyl nitroxide radicals as valuable bridging ligands for obtaining low-dimensional, strongly coupled magnetic systems have attracted much attention [9,10]. On the other hand, NITR substituted ligands have a unique combination of chemical stability and versatility that makes them attractive candidates for spin labels and paramagnetic building blocks [11,12].

Compared with extensive investigations of the magnetic coupling between transition metal complexes with organic radicals, there are little reports for the magnetic interactions in Ln–radical complexes, except the Gd(III) with organic radicals. It is owing to the orbital contribution arising from the ground state splitting into Stark sublevels from the $^{2S+1}L_J$ spectroscopic energy terms due to the crystal field perturbation, or the violation of the Curie law corresponding to a depopulation of the sublevels. It prompt us to extend the study to the other lanthanide ions to gain some information concerning magnetic interaction between Ln(III) ion and radicals.

To develop the new magnetic coupling systems of 4f-radicals and better understand the nature of 4f–2p magnetic interaction, using a new radical NITPh-p-Cl and rare-earth metal ions, we have synthesized two rare-earth-radical complexes: $\{Ln(hfac)_3(NITPh\text{-}p\text{-}Cl)_2\}$ (Ln = Gd (**1**), Nd(**2**)). Their crystal structures and magnetic properties were described in this paper. Herein the synthesis, X-ray structures and magnetic properties of those complexes are reported.

2. Experimental

2.1. General

All reagents were purchased from commercial sources and were used as received. Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Model 240 Perkin–Elmer elemental analyzer. The infrared spectra were recorded on a Shimadzu IR spectrophotometer model 408 in the 4000–600 cm^{-1} region, using KBr pellets. Temperature dependent magnetic susceptibilities were measured on a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

2.2. Synthesis

NITPh-p-Cl: 2-(4′-chlorphenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide was prepared following the literature method [13,14].

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A solution of Gd(hfac)$_3$·2H$_2$O (80 mg, 0.1 mmol) in 10 mL of dry *n*-heptane was heated under reflux for 20 min. After that, the solution was cooled to 65 °C, and a solution of NIT Ph-p-Cl (52 mg, 0.2 mmol) in 3 mL of CH$_2$Cl$_2$ was added. The resulting mixture was stirred for 30 min and then cooled to room temperature. After filtration, the resulting solution was stored in a refrigerator at 5 °C. After 2 days, dark blue crystals of **1** were collected. *Anal.* Calc. for $C_{41}H_{35.5}Cl_{2.5}F_{18}N_4O_{10}Gd$: C, 39.52; H, 2.61; N, 4.15. Found: C, 36.97; H, 2.69; N, 4.21%. The IR(KBr) spectrum displays weak broad band at 3423 cm, assigned to the absorption of O–H group, a strong broad band at 1632, 1517, attributed to the $\nu_{C=O}$ stretching vibrations. The weak band observed at 1344 and 1185 cm^{-1} is assigned to the absorption of N–O group of NIT Ph-p-Cl.

Blue crystal of **2** were prepared in a manner similar to that of **1** by replacing Gd(hfac)$_3$·2H$_2$O with Nd(hfac)$_3$·2H$_2$O. Dark blue crystals of **2** were collected. *Anal.* Calc. for $C_{44}H_{42}Cl_2F_{18}N_4O_{10}Nd$: C, 43.51; H, 3.42; N, 4.61. Found: C, 44.05; H, 3.53; N, 4.67%. The IR(KBr) spectrum displays weak broad band at 3308 cm, assigned to the absorption of O–H group, a strong broad band at 1609, 1506, attributed to the $\nu_{C=O}$ stretching vibrations. The weak band observed at 1323, 1185 cm^{-1} is assigned to the absorption of N–O group of NIT Ph-p-Cl.

2.3. X-ray crystallographic study

Single crystal X-ray diffraction measurements were carried out on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected at room temperature by φ–ω scan technique in the range 1.59° ⩽ θ ⩽ 25.02°. The collected data were reduced by using the program SAINT [15] and empirical absorption correction was done by using the SADABS program [16]. The structure was solved with direct methods using SHELXS-97 [17]. The H atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [18]. All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters; $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = \sum[w(|F_o|^2 - |F_c|^2)^2]/\sum[w(|F_o|^2)^2]^{1/2}$, respectively. Crystal data and selected structural parameters are summarized in Tables 1 and 2, respectively.

3. Results and discussion

3.1. Description of the crystal structures

Complexes **1** and **2** possess similar structures, complex **1** is chosen for the description of the structure of complex. The symmetric unit of complex **1**, as shown in Fig. 1, consists of a discrete adduct Gd(hfac)$_3$(NITPh-p-Cl)$_2$. A central Gd(III) atom is eight-coordination sites which are occupied by six oxygen atoms from three hfac ligands, two oxygen atoms from two nitroyl nitroxide radicals. The bond distances between the Gd(III) ions and the oxygen atoms of the hfac ligands are in the range of 2.345(4)–2.410(4) Å, while Gd–O (nitronyl nitroxide) bond distance is 2.344(4) and 2.357(4) Å. All the Gd–O bond distances are comparable to the other complexes [19,20]. The radical behaves as a monodentate ligands through one oxygen atom of nitronyl nitroxide, while the other oxygen atom of nitronyl nitroxide remains uncoordinated, the bond distances of uncoordinated N–O (1.265(6) Å) are shorter than the coordinated ones (1.303(5) Å). The ONCNO moiety is almost planar, with a mean deviation 0.0156 Å from the least-squares plane. The dihedral angles between the nitronyl nitroxide moiety and the benzene ring are 39.4°.

Table 1
Crystal data and details of experiment for compounds **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{41}H_{35.5}Cl_{2.5}F_{18}N_4O_{10}Gd$	$C_{44}H_{42}Cl_2F_{18}N_4O_{10}Nd$
Formula weight	1332.11	1343.96
T (K)	113(2)	113(2)
λ (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	11.439(2)	11.463(2)
b (Å)	12.794(3)	12.882(3)
c (Å)	19.269(4)	19.266(4)
α (°)	91.20(3)	90.80(3)
β (°)	105.50(3)	106.00(3)
γ (°)	95.18(3)	95.30(3)
V (Å^3)	2703.4(9)	2720.7(10)
Z	2	2
D_{calc} (mg/m^3)	1.636	1.641
Absorption coefficient (mm^{-1})	1.466	1.170
F(0 0 0)	1316	1340
Crystal size (mm^3)	0.24 × 0.20 × 0.16	0.22 × 0.20 × 0.18
θ Range for data collection (°)	2.33–25.02	1.59–25.02
Reflections collected/unique (R_{int})	19 821/9465 (0.0711)	19 925/9535 (0.0298)
Data/restraints/parameters	9465/318/829	9535/231/776
Goodness-of-fit on F^2	0.987	1.097
$R_1[I > 2\sigma(I)]$	0.0561	0.0337
$wR_2[I > 2\sigma(I)]$	0.1446	0.0935
R_1 (all data)	0.0625	0.0366
wR_2 (all data)	0.1514	0.0955

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

Compound **1**			
Bond lengths			
Gd(1)–O(1)	2.344(4)	Gd(1)–O(5)	2.379(4)
Gd(1)–O(8)	2.345(4)	Gd(1)–O(7)	2.386(4)
Gd(1)–O(3)	2.357(4)	Gd(1)–O(6)	2.393(4)
Gd(1)–O(10)	2.366(4)	Gd(1)–O(9)	2.410(4)
Bond angles			
O(1)–Gd(1)–O(8)	93.60(14)	O(5)–Gd(1)–O(7)	126.80(15)
O(1)–Gd(1)–O(3)	137.35(14)	O(1)–Gd(1)–O(6)	73.69(13)
O(8)–Gd(1)–O(3)	99.40(14)	O(8)–Gd(1)–O(6)	147.43(15)
O(1)–Gd(1)–O(10)	102.77(14)	O(3)–Gd(1)–O(6)	73.68(13)
Compound **2**			
Bond lengths			
Nd(1)–O(3)	2.394(2)	Nd(1)–O(10)	2.428(2)
Nd(1)–O(6)	2.396(2)	Nd(1)–O(5)	2.440(2)
Nd(1)–O(1)	2.405(2)	Nd(1)–O(9)	2.445(2)
Nd(1)–O(8)	2.413(2)	Nd(1)–O(7)	2.469(2)
Bond angles			
O(3)–Nd(1)–O(6)	94.49(9)	O(10)–Nd(1)–O(5)	127.39(8)
O(3)–Nd(1)–O(1)	138.09(8)	O(3)–Nd(1)–O(9)	74.14(8)
O(6)–Nd(1)–O(1)	98.17(9)	O(6)–Nd(1)–O(9)	147.48(8)
O(3)–Nd(1)–O(8)	103.15(8)	O(1)–Nd(1)–O(9)	73.85(9)

For complex **2**, the structure is very similar to the complex **1** except for the substitution of Gd(III) ion with Nd(III) ion (see Supplementary material), which makes the bond distances and angles different. The Nd–O$_{Rad}$ bond lengths are 2.394(2) and 2.405(2) Å, while the Nd–O bond distance with the hfac ligands are in the range 2.396(2)–2.469(2) Å. The ONCNO moiety of the radical is almost planar, with a mean deviation 0.0054 Å from the least-squares plane, indicating the easy delocalization of the free