



Syntheses, structure, magnetic and thermodynamics property of novel lanthanide complexes with nitronyl nitroxide radical



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ABSTRACT

Four new nitronyl nitroxide radical-Ln(III) complexes, Ln(hfac)₃(NITPhSCF₃)₂ (Ln(III) = Sm(**1**), Gd(**2**), Tb(**3**), Dy(**4**); NITPhSCF₃ = 2-(4-trifluoromethylthiophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide; hfac = hexafluoroacetylacetonate), have been synthesized and characterized. They are isostructural, which show mononuclear tri-spin structures. The central Ln(III) ion is eight-coordinated by three hfac anions and two NITPhSCF₃ molecules. Direct-current magnetic study shows that there exist ferromagnetic interactions between Gd(III) ion and radicals (NITPhSCF₃) with $J_{\text{Gd-Rad}} = 1.61 \text{ cm}^{-1}$, and antiferromagnetic interactions between radicals with $J_{\text{Rad-Rad}} = -2.83 \text{ cm}^{-1}$ in complex **2**. The magnetic analysis with the rough approximate model show that a ferromagnetic coupling exists between Tb(III) and radical in **3**, while a antiferromagnetic coupling between Dy(III) and radical in **4**. The thermodynamics properties of four complexes were studied with differential scanning calorimetry (DSC), such as heat capacity, thermodynamic functions ($H_T-H_{298.15K}$), ($S_T-S_{298.15K}$), and ($G_T-G_{298.15K}$).

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1. Introduction

The nitronyl- and imino-nitroxide radicals (NITR and IMR) have become interesting building blocks for molecule-based magnetic materials in the last decades, based their paramagnetic property, the versatile chemical modification and stability under ambient conditions [1]. The early strategies were focused on the design of transition metals–radical complexes, which expect to obtain 3D molecular-based magnets below a critical temperature (T_C) [2–4]. According the ferrimagnetic principle, Mn(II) is the most ideal ion because the Mn(II)–radical interaction is very strong and the resulting spin is also large [4–9]. In these works, the subtle changes of R substituents for NITR and IMR radicals greatly influence not only their coordination ability and coordination mode, but also the molecule structure, crystalline structure and the ultimate magnetic property of metal–radical complexes.

Since the discovery of first single-chain magnet [Co(hfac)₂(-NITPhOMe)] by D. Gatteschi [10], lanthanide–radical approach has become an effective method to obtain the slow-relaxing molecular

units, such as single chain magnets (SCMs) [11–15] and single molecule magnets (SMMs) [16–26]. The strong spin-orbit coupling and large magnetic anisotropy of most Ln(III) ions are the key factors in the design strategies. These superparamagnetic molecular units could be used as potential candidates for high-density information storage devices and quantum computers in the future [27–29]. Up to now, numerous investigations about Ln(III)–radical complexes have been performed, in which the slow magnetic hysteresis, blocking temperature, energy barrier and magnetic interactions between spin carriers, are closely related to the different R substituents of radical ligands. Therefore, it is very important to design and prepare more new radicals and their Ln(III)–radical complexes. In this paper, we use a new nitronyl nitroxide radical NITPhSCF₃ (4-trifluoromethylthiophenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) as radical ligand to coordinate with Ln(III). Four mononuclear lanthanide–radical complexes Ln(hfac)₃(NITPhSCF₃)₂ (Ln(III) = Sm(III) **1**, Gd(III) **2**, Tb(III) **3**, Dy(III) **4**) have been successfully obtained. Their single-crystal structure and magnetic property are studied. Moreover, their basic heat capacity (C_p) is a key thermophysical data, and the thermodynamic functions such as enthalpy, entropy, and Gibbs energy are important for both theoretical and practical purposes. So the C_p and basic thermodynamic functions are also studied.

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2. Experimental

2.1. Materials and instruments

All of the reagents used in the syntheses are of analytical grade and without further purification. The hexafluoroacetylacetone, 4-(trifluoromethylthio)benzaldehyde were purchased from J&K Chemical Company. Syntheses of Ln(hfac)₃·2H₂O (Ln(III) = Sm(III), Gd(III), Tb(III), Dy(III)) and radical NITPhSCF₃ have been performed according to the literature methods [30,31].

Elemental analyses for C, H, N were carried out on a Model 1112 Flash EA elemental analyzer. IR spectra were recorded in the region 400–4000 cm⁻¹ on a FT-IR-8900 spectrophotometer with samples as KBr disks. The heat capacities were measured by a NETZSCH DSC 200 F3 differential scanning calorimetry. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS XL7 magnetometer in the temperature range of 2.0–300 K with an applied magnetic field of 1000 Oe. Diamagnetism contributions of all the constituent atoms were corrected by using the Pascal's constants.

2.2. Syntheses of Ln(hfac)₃(NITPhSCF₃)₂ (Ln = Sm(1), Gd(2), Tb(3), Dy(4))

All of the four complexes were synthesized by the same method. Herein, only the synthesis of complex **1** is described in detail [32–34]. Sm(hfac)₃·2H₂O (0.03 mmol) was dissolved in *n*-heptane (20 mL) and refluxing for 0.5 h. Then, the solution was cooled to 60 °C, to which a solution of NITPhSCF₃ (0.06 mmol) in CH₂Cl₂ (5 mL) was added. The blue-purple mixed solution was refluxed for 0.5 h, and then cooled to room temperature. After filtration, the filtrate was allowed to stand at room temperature. Red-brown crystals suitable for X-ray structure analysis were obtained by the slow evaporation of filtrate for about 3 days. Complexes **2** to **4** were synthesized in the similar process using Ln(hfac)₃·2H₂O (Ln(III) = Gd(III), Tb(III), Dy(III)) instead of Sm(hfac)₃·2H₂O.

Anal. Calc (**1**) for C₄₃H₃₅F₂₄SmN₄O₁₀S₂: C, 35.91%; H, 2.45%; N, 3.90%. Found: C, 35.79%, H, 2.53%, N, 3.80%. IR(KBr cm⁻¹): 1653(vs), 1533(s), 1506(s), 1349(s), 1258(vs), 1203(s), 1148(s), 1085(w); Anal. Calc (**2**) for C₄₃H₃₅F₂₄GdN₄O₁₀S₂: C, 35.74%; H, 2.44%; N, 3.88%. Found: C, 34.74%, H, 2.35%, N, 3.67%. IR(KBr cm⁻¹): 1651(vs), 1557(s), 1506(s), 1350(s), 1258(vs), 1204(s), 1146(s), 1084(w); Anal. Calc (**3**) for C₄₃H₃₅F₂₄TbN₄O₁₀S₂: C, 35.70%; H, 2.44%; N, 3.87%. Found: C, 35.54%, H, 2.49%, N, 3.71%. IR(KBr cm⁻¹): 1653(vs), 1559(s), 1506(s), 1350(s), 1258(vs), 1204(s), 1146(s), 1084(w); Anal. Calc (**4**) for C₄₃H₃₅F₂₄DyN₄O₁₀S₂: C, 35.61%; H, 2.43%; N, 3.86%. Found: C, 35.43%, H, 2.30%, N, 3.91%. IR(KBr cm⁻¹): 1653(vs), 1559(s), 1508(s), 1348(s), 1258(vs), 1204(s), 1144(s), 1084(w).

2.3. Crystal structure determination

Determination of the unit cell and data collection for the complexes were performed with Mo K α radiation ($\lambda = 0.71073$ Å) on a SMART APEX II CCD area detector. All of the structures were solved primarily by direct methods and refined by the full-matrix least squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter [35,36]. Crysta data and details of structural determination refinement are summarized in Table 1. The selected bond lengths and angles of complex **1** are listed in Table 2, and the others are listed in Tables S1–S3 in the Supporting Information.

3. Result and discussion

3.1. Description of the crystal structures

Single-crystal X-ray diffraction analysis revealed that the complexes Ln(hfac)₃(NITPhSCF₃)₂ (Ln(III) = Sm(**1**), Gd(**2**), Tb(**3**), Dy(**4**)) are isostructural, which crystallize in monoclinic *P*2₁/*c* space group. They all exhibit mononuclear tri-spin rad-Ln(III)-rad structures, in which the nitronyl nitroxide radicals act as monodentate ligands towards Ln(III) ion through the oxygen atom of N–O group, and each central Ln(III) ion is eight-coordinated. The molecular structure of complex **1** is shown in Fig. 1, and that of **2** to **4** are shown in Figs. S1–S3 in the Supporting Information. The Sm(hfac)₃(NITPhSCF₃)₂ (**1**) is used as an example to describe their structural characteristics. The Sm(III) ion is eight coordinated by six oxygen atoms from three hfac ligands, with the Sm–O bond lengths in the range of 2.363(6) Å to 2.435(6) Å, the other two oxygen atoms are from two NITPhSCF₃ radicals, with the Sm–O bond lengths of 2.396(6) Å and 2.374(5) Å. The analysis of the coordination polyhedron around Sm(III) ion indicates a distorted triangular dodecahedron (Fig. 2) [37]. The coordinated N1–O1 and N3–O3 bond lengths of 1.287(8) Å and 1.312(8) Å are a little larger than the uncoordinated N2–O2 and N4–O4 bond lengths of 1.267(8) Å and 1.305(8) Å, and the bond angle of O3–Sm1–O1 is 139.72(19)°. These structural characteristics is similar to that of the analogous Ln(III)-NITR complexes in literature, of which the N–O distances are within the range of 1.26–1.33 Å [38–40]. The packing diagram for complex **1** is shown in Fig. 3. There shows no hydrogen bonding or $\pi \cdots \pi$ stacking interaction among the molecules in the system. The shortest intermolecular distance of uncoordinated oxygen atoms of the N–O groups is 3.224 Å, and the nearest distance of Sm \cdots Sm between the adjacent molecules is 11.118 Å.

For the other complexes, the replacement of the central Ln(III) ions results in the crystal parameters, bond lengths and bond angles vary somewhat. The selected bond lengths and bond angles are listed in Tables S1–S3 in the supporting Information.

3.2. Magnetic properties

3.2.1. Magnetic properties for Sm(1)

Fig. 4 shows the temperature dependence of the magnetic susceptibility for complex **1**. The $\chi_M T$ value is 1.10 cm³ K mol⁻¹ at room temperature, which is a little higher than 0.839 cm³ K mol⁻¹ expected for one uncoupled Sm(III) (⁶H_{5/2}, $g = 2/7$, $\chi_M T = 0.089$ cm³ K mol⁻¹) plus two organic radicals ($S = 1/2$, $g = 2.0$, $\chi_M T = 0.375$ cm³ K mol⁻¹). As temperature cooling, the $\chi_M T$ value decrease gradually and reaching a minimum of 0.14 cm³ K mol⁻¹ at 2 K. The ⁶H ground term for the Sm(III) ion is split by the spin–orbit coupling into six levels $E(J) = \lambda J(J + 1)/2$ ($J = 5/2, 7/2, 9/2, 11/2, 13/2, \text{ and } 15/2$) with the spin–orbit coupling parameter λ on the order of 200 cm⁻¹. In addition to the ground state ⁶H_{5/2}, the first excited state ⁶H_{7/2} and even higher excited states can be considerably populated at room temperature [18], so the $\chi_M T$ value at room temperature is higher than the expected theoretical value. With the approximately model [18], the data have been tried to fit for a rough quantitative estimate of the magnetic interaction parameters between paramagnetic species, but failed.

Based on the $\chi_M T$ curve, the decrease of $\chi_M T$ value on lowering the temperature attributes to the thermal depopulation of these excited levels of Sm(III), the interaction between the paramagnetic species (Sm(III) ion and radicals), and the crystal field splitting. Refer to the Sm(III)-radical complex [18], The interaction between the paramagnetic species should be antiferromagnetic.

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