

A Gadolinium(III) complex based on Nitronyl nitroxide ligand exhibiting magnetic relaxation process

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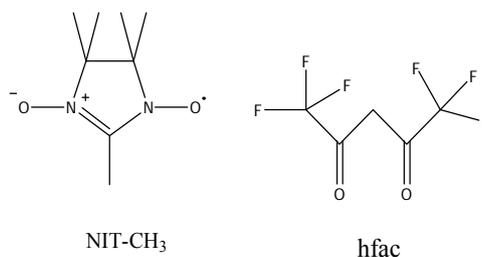
Abstract. Reaction of the nitronyl nitroxide radical NIT-CH₃ with Gd(hfac)₃ affords a one-dimensional lanthanide–nitronyl nitroxide compound: [Gd(hfac)₃(NIT-CH₃)_n] (1) Single crystal X-ray crystallographic analysis reveals that this compound is one-dimensional chain built up by Gd(hfac)₃ units bridged by radicals through their NO groups. DC magnetic susceptibilities indicate that Gd complex paramagnetic above 2.0 K.

1. Introduction

Due to their potential applications in high-density information storage and quantum spintronic devices, a lot of attention has been paid to the design and construction of one-dimensional single-chain magnets (SCMs) [1–3]. SCMs are characterized as slow magnetization relaxation caused by the association of large ground state spin (S_T) value with a significant uniaxial (Ising-like) magnetic anisotropy (D), which leads to a significant energy barrier to magnetization reversal (U). These kind of one-dimensional complexes can be observed magnetic hysteresis arising from slow dynamics of the magnetization of a pure 1D structure rather than 3D magnetic ordering [4].

Previous studies show that lanthanide (III) ions are good candidates for the construction of SCMs, owing to their significant magnetic anisotropy from the large and unquenched orbital angular momentum. However, the drawback for lanthanide(III) ions is the naturally accompanying quantum tunneling from the hyperfine couplings and dipolar spin–spin interactions of lanthanide ions, which always lowers the effective relaxation energy barrier and induces the loss of remnant magnetization [5]. Fortunately, exchange interactions which generally exist in molecular paramagnetic species have been proved to be an effective method to reduce quantum-tunneling relaxation and then might increase the effective relaxation energy barrier processes. One of the challenges of using this approach in lanthanide based SCMs is that the limited radial extension of the 4f orbital always induces weak exchange interactions. In 2011 Long research group indicated that the N_2^{3-} radical ligands can effectively transfer the magnetic interactions between lanthanide ions. This strong exchange coupling between anisotropic metal and radical ligand generally leads to SCMs with high relaxation energy barrier [6].

Nitronyl nitroxides are used widely as bridging ligands to construct one-dimensional systems because they possess two identical N–O coordination groups, which can be coordinated to two different metal ions and contribute to compounds with one-dimensional structures. Moreover, stable radical ligands can transfer the effective magnetic interactions. Recently, SCM behavior has been observed in some nitronyl nitroxide-Co(II)/Ln(III) one-dimensional compounds, and some of them show relative high energy barrier. It's worth noting that these reported SCMs are base on aromatic group substituted nitronyl nitroxides [7-8], further research of SCMs base on aliphatic group substituted nitronyl nitroxides is necessary. In order to further explore the relationship between the magnetic properties and substitution of the radical ligands, we report one one-dimensional complex [Gd(hfac)₃(NIT-CH₃)_n] (1) (NIT-CH₃ = 2,4,4,5,5-pentamethylimidazolyl-1-oxyl-3-oxide). Magnetic studies indicate that this Gd complex paramagnetic above 2.0 K.



Scheme 1. Molecule structure of NIT-CH₃ and hfac.

2. Experimental Section

2.1 Synthesis of [Gd(hfac)₃(NIT-CH₃)₃]_n.

A solution of Gd(hfac)₃·2H₂O (0.0814 g 0.1 mmol) in 30 mL dry boiling n-heptane was heated to reflux for about 1.5 h. Then the solution was cooled to 60 °C, a solution of NIT-CH₃ (0.0171 g 0.1 mmol) in 2 mL of CH₂Cl₂ was added. The resulting solution was stirred for 1 min and cooled to room temperature. After about two days, red crystals suitable for single-crystal X-ray analysis were collected, yield 47 %. Anal. Calc. for C₂₃H₁₈F₁₈N₂O₈Gd (949.63): calcd. C 29.09, H 1.91, N 2.95 %; found C 29.41, H 1.98, N 3.02 %. FT-IR (KBr): 1653 (s), 1618 (s) 1559 (s), 1532 (s), 1258 (s) 1205 (s), 1147 (s), 801 (m), 661(m) cm⁻¹.

2.2 X-ray crystal structure determinations

X-ray single-crystal diffraction data for all four complexes were collected using a Bruker APEX-II CCD diffractometer at 173 K equipped with graphite-monochromated Mo/K α radiation (λ =0.71073 Å). The structures were solved by direct methods by using the program SHELXS-97 and refined by full-matrix least-squares methods on F^2 with the use of the SHELXL-97 program package. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Disordered C and F atoms were observed for all compounds. The restraints of SPLIT, DELU and ISOR were applied to keep the disordered molecules reasonable. CCDC: 1548423, **1**

3. Results and discussion

3.1 Structural descriptions

As shown in Figure 1, complex **1** crystallizes in $P2_1/n$ space group with a monoclinic crystal system. The [Gd(hfac)₃] units are connected by NIT-CH₃ to form a one-dimensional infinite Gd(III)–NIT-CH₃ chain. There is only one crystallographically independent Gd(hfac)₃(NIT-CH₃) moiety in the asymmetric unit. The nitroxide ligands which connect to the same Gd(III) are trans and the angle of O_{rad}–Gd–O_{rad} is found to be 131.10°. The Gd–O(radical) bond lengths are 2.370 Å and 2.388 Å, respectively. The Gd–O(hfac) distances are in the range of 2.358–2.378 Å. The nearest intrachain Gd·Gd distances are found to be 8.194 Å for complex **1**.

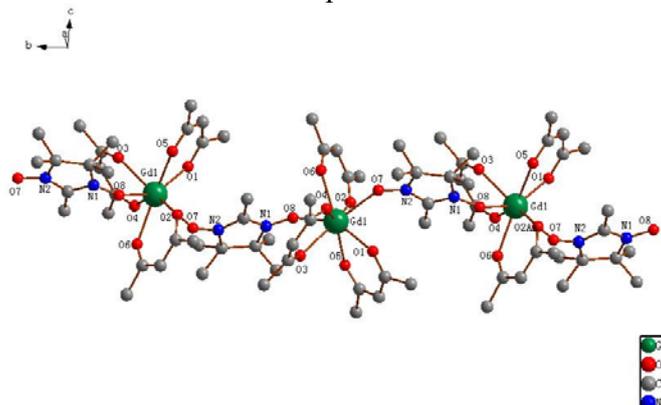


Fig. 1 One-dimensional chain structure of complex **1** with the atom-labeling scheme. All hydrogen and fluorine atoms have been omitted for clarity.

3.2 Magnetic properties

To study the static magnetic properties of complex **1**, variable-temperature magnetic susceptibilities were measured from 300 K to 2 K in an applied field of 1 kOe. The $\chi_M T$ vs. T plots for **1** are shown in Figure 2 left. At 300 K, the $\chi_M T$ value is $8.21 \text{ cm}^3 \text{ K mol}^{-1}$, close to the theoretical value of uncoupled Gd^{III} ion $8.26 \text{ cm}^3 \text{ K mol}^{-1}$ which equal to $7.88 \text{ cm}^3 \text{ K mol}^{-1}$ (f^7 electron configuration) plus $0.375 \text{ cm}^3 \text{ K mol}^{-1}$ (one organic radical $S = 1/2$). Upon cooling to 50 K, a slow increase of $\chi_M T$ value to $8.33 \text{ cm}^3 \text{ K mol}^{-1}$ was observed, then $\chi_M T$ increases rapidly to the value of $9.92 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. This increase of $\chi_M T$ from 300 K to 2 K indicates ferromagnetic interaction in the molecule.

The field dependence of magnetization of complex **1** has been determined at 2 K in the range of 0–70 kOe (Figure 2 right). With increasing the applied field, M increases up to $7.19 N\beta$ at 70 kOe without reaching saturation. This may be attributed to the presence of magnetic anisotropy in the system.

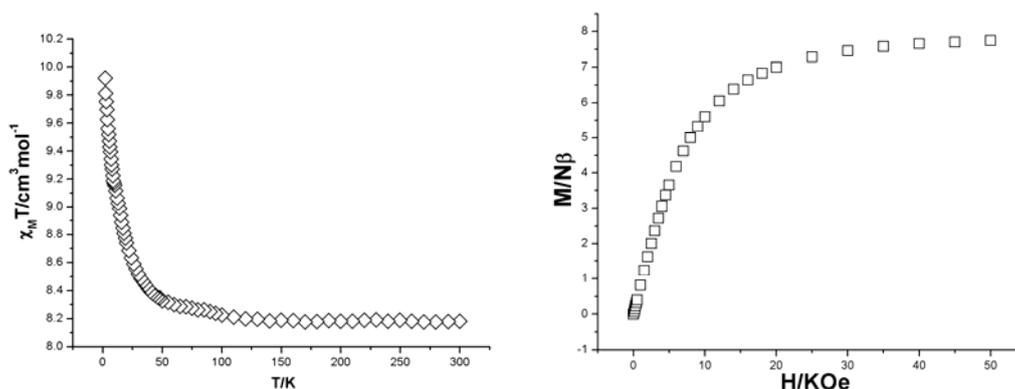


Fig. 2 Temperature dependence of $\chi_M T$ for complex **1** (left) and field dependence of magnetization of complex **1** at 2.0 K (right).

4. Summary

In this paper, we have successfully obtained a one-dimensional Gd-radical complex base on Gd and aliphatic group substituted nitronyl nitroxides. Magnetic studies reveal that this complex paramagnetic above 2.0 K.

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