One-dimensional lanthanide chain bridged by nitronyl nitroxide radical ligand: structure and magnetic properties

Hui Yang Dong and Me Zhu*

Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, Zhejiang, 310018, China

Abstract. In order to synthesize the molecular magnetic material, the complex \([\text{Nd(hfac)}(\text{NIT-5MeThien})]_{n}\) was synthesized by the reaction using radical ligand and \(\text{Nd(hfac)} \cdot 2\text{H}_2\text{O}\). X-ray diffraction analysis showed that the compound belongs to the monoclinic system and constituted by \(\text{Nd(hfac)}\) and NIT-5MeThien to obtain a one-dimensional chain which nitroxide radical acted as a bridged ligand through the N-O groups. Variable temperature magnetization of complex was shown the antiferromagnetic interaction between Nd(III) ion and nitroxide radical.

1 Introduction

Molecular ferromagnetic materials have gained increasing interest in the last three decades due to their high performance of magnetic properties. It has a wide range of applications, for example, high-density information storage; coating of stealth fighter and so on.\([1-7]\) The emergence of molecular-based materials began with the exploration of theory. First of all, McConnel\([8]\) propose that ferromagnetism can exist in organic compounds and the mechanism of intermolecular ferromagnetic coupling. Meanwhile, the first molecular-based magnets \([\text{Fe(dtc)}_2\text{Cl}]\) were obtained by Wickman\([9]\). Then, more and more magnets were prepared by various methods. Among these ways, direct coordination of nitronyl nitroxide radicals to metal ions also has a place. Nitronyl nitroxide radical have played an important role in the design and synthesis of molecular magnets due to their nice stability and easy to modify. A. Caneschi et al.\([10]\) first reported a one-dimensional chain molecular ferromagnet \([\text{Ni(hfac)}_2(\text{NITMe})]\). Magnetic studies show that there was a strong antiferromagnetic interaction between nickel and NO groups of nitronyl nitroxide radical. And subsequent research show that Ln ions have strong magnetoanisotropy\([11-16]\), so lanthanide-magnet have attracted attention from researchers.

In this paper, we design a new nitronyl nitroxide radical \(\text{NIT-5MeThien}\) (Scheme 1), and gained \([\text{Nd(hfac)}(\text{NIT-5MeThien})]\) by using this nitronyl nitroxide radical to react with \(\text{Nd(hfac)}\) ion. The variable-temperature magnetic susceptibility shown that the coordinated radical ligands and Nd(III) ion exist antiferromagnetic couplings.

2 Experimental section

2.1. Materials and physical measurements

All the chemical reagents used in the experiment were analytically pure, NIT-5MeThien were synthesized based on methods in the literature.\([17]\) Perkin-Elmer 240 elemental analyzer was used for element analyses (C, H and N). Infrared spectra data was derived from Bruker TENOR 27 spectrometer in the range of 400 to 4000 cm\(^{-1}\) (KBr pellets). Powder X-ray diffraction (PXRD) data of complex was obtained by a Rigaku Ultima IV diffractometer.

2.2. Synthesized of \([\text{Nd(hfac)}(\text{NIT-5MeThien})]\)

The complex is synthesized according to the following process. \(\text{Nd(hfac)} \cdot 2\text{H}_2\text{O} (0.02\text{mmol})\) was dissolved in boiling dry n-heptane (10ml) and kept under reflux at 103 °C for two hours. Then the solution was cooled down to 90 °C, after which a solution of NIT-5MeThien (0.002mmol) in 5 mL of CH\(_2\)Cl\(_2\) was introduced slowly. The mixture solution keep stirring for 15 min at 90 °C. After that, the mixture solution was cooled down to room temperature and filtered. Two days later, the green bars crystals which was suitable for X-ray diffraction was obtained.

* Corresponding author: zhumei0321@163.com
[Nd(hafc)₄(NIT-5MeThien)] Yield 46 %; C₂₇H₂₃F₁₈Nd₂O₈N; Elem. anal. (%) found: C, 31.46; H, 2.13; N, 2.45; Calcd: C, 31.83; H, 1.98; N, 2.75. FT-IR(KBr, cm⁻¹): 3439 (w), 1654 (s), 1377 (w), 1350 (m), 1258 (s), 1212 (s), 1147 (s), 802 (m), 662 (m).

2.3. X-ray data collection and structure refinement

A Rigaku Saturn CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173 K was used to get crystallographic data. The structure of complex was solved by direct methods and refine by full-matrix least-squares techniques against F² with the SHELXS-97 and SHELXTL-97[18-19] program package. All hydrogen atoms were added geometrically at proper positions, and non-hydrogen atoms were refined anisotropically. Significant crystallographic data and structural refinement are included in Table 1. The important bond lengths (Å) and angles (°) are list in table 2 and table 3.

Table 1. Crystallographic data and structure refinement for complex

| Bond       | Dist.(Å) |
|------------|----------|
| Nd(1)-O(1) | 2.400(3) |
| Nd(1)-O(2) | 2.416(3) |
| Nd(1)-O(3) | 2.394(4) |
| Nd(1)-O(4) | 2.431(3) |
| Nd(1)-O(5) | 2.406(4) |
| Nd(1)-O(6) | 2.453(3) |
| Nd(1)-O(7) | 2.415(3) |
| Nd(1)-O(8) | 2.481(3) |

Table 2. The important bond distances (Å) for complex

| Angle                  | (°)   |
|------------------------|-------|
| O(7)-Nd(1)-O(1)        | 95.46(12) |
| O(7)-Nd(1)-O(2)        | 144.96(12) |
| O(7)-Nd(1)-O(3)        | 78.81(12) |
| O(7)-Nd(1)-O(4)        | 73.94(11) |
| O(7)-Nd(1)-O(5)        | 92.88(12) |
| O(7)-Nd(1)-O(6)        | 72.08(12) |
| O(7)-Nd(1)-O(8)#3      | 142.27(11) |
| O(1)-Nd(1)-O(8)#3      | 107.04(11) |

3 Results and discussion

3.1. Description of the crystal structures

Single crystal X-ray diffraction data manifest that complex was crystallize in the monoclinic space group P₂₁/c. Figure 1 shows the structure which is one-dimensional chain. As depicted in figure 1, the Nd(III) mental ion is eight-coordinated by two NO units of two radicals and six oxygen atoms of three hfac anions. The Nd-O(radical) distance range from 2.394 to 2.476 Å, which is basically consistent with previous reports.[20] The Orad-Nd-Orad angle is 142.27(11)°. The shortest Nd---Nd distance is 8.709 Å in the chain, Figure 2 shows that the shortest interchain Nd---Nd separation is 11.190 Å.
3.2. Magnetic properties

The variable-temperature magnetic susceptibility data for complex was investigated under a dc field of 1000 Oe at 2–300 K (figure 3). At room temperature, the value of $\chi_M$ is $3.71 \text{ cm}^3 \text{ K mol}^{-1}$. It is slightly lower than $4.03 \text{ cm}^3 \text{ K mol}^{-1}$ which is the theoretical value of spin alone for two uncoupled Nd(III) ions ($^{4}I_{9/2}$) and two uncoupled radicals (S = 1/2). As temperature goes down, the value of $\chi_M$ achieves a minimum of $0.96 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The reason why $\chi_M$ decreases with temperature is that the exchange coupling between the Nd(III) ion and the NO radicals is antiferromagnetic. In the temperature range of 45-300 K, the relationship between $\chi_M^{-1}$ and T conforms to the Curie-Weiss law. Subsequently, a negative Weiss constant of $\theta = -19.65 \text{ K}$ and the Curie constant of $C = 3.58 \text{ cm}^3 \text{ K mol}^{-1}$ can be calculated by linear fitting. These data further proved that there is an antiferromagnetic interaction between the rare earth (Nd(III)) ion and the ligand (NO).

4 Conclusions

In summary, we have successfully obtained one-dimensional chain molecular magnets. In this complex, Nd(III) ions are bridged by nitronyl nitroxide radicals through the NO groups. The magnetic studies show that there is antiferromagnetic between Nd(III) ions and NO groups of nitronyl nitroxide radical.

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