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

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Abstract. In order to synthesize the molecular magnetic material, the complex $\{Nd(hfac)_3(NIT-5MeThien)\}_n$ ($NIT-5MeThien=2-(5-Methyl-2'-thienyl)-5--4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide$) has been synthesized by the reaction using radical ligand and $Nd(hfac)_3 \cdot 2H_2O$. X-ray diffraction analysis showed that the compound belongs to the monoclinic system and constituted by $Nd(hfac)_3$ 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, McConnell^[8] propose that ferromagnetism can exist in organic compounds and the mechanism of intermolecular ferromagnetic coupling. Meanwhile, the first molecular-based magnets $[Fe(dtc)_2Cl]$ 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 $[Ni(hfac)_2(NITMe)]$. 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-magnets have attracted attention from researchers.

In this paper, we design a new nitronyl nitroxide radical $NIT-5MeThien$ (Scheme 1), and gained $[Nd(hfac)_3(NIT-5MeThien)]$ by using this nitronyl nitroxide radical to react with $Nd(III)$ ion. The variable-temperature magnetic susceptibility shown that the coordinated radical ligands and $Nd(III)$ ion exist antiferromagnetic couplings.

Scheme 1 NIT-5MeThien

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. Synthesis of $[Nd(hfac)_3(NIT-5MeThien)]$

The complex is synthesized according to the following process. $Nd(hfac)_3 \cdot 2H_2O$ (0.02mmol) 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_2Cl_2 was introduced slowly. The mixture solution kept 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.

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[Nd(hfac)₃(NIT-5MeThien)] Yield 46 % ;
C₂₇H₂₀F₁₈N₂NdO₈S; 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 K α radiation ($\lambda = 0.71073$ Å) at 173 K was used to get crystallographic data. The structure of complex was solved by direct methods and refined 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

Formula	C ₂₇ H ₂₀ F ₁₈ N ₂ NdO ₈ S
Formula weight	1018.76
T(K)	113(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	P ₂₁ /c
Unit cell dimensions	a=21.041(6) Å $\alpha = 90$ deg. b=17.417(4) Å $\beta = 116.250(4)$ deg. c=22.667(6) Å $\gamma = 90$ deg.
Volume (Å ³)	7450(3)
Z	8
Calculated density (mg/m ³)	1.817
Absorption coefficient (mm ⁻¹)	1.587
Crystal size (mm ³)	0.23 x 0.20 x 0.18
θ range for data collection (°)	1.54 to 27.91
Unique reflns/ R_{int}	75772 / 17706 [R(int) = 0.0634]
Completeness to $\theta = 25.01$	99.5 %
Max. and min. transmission	1.000 and 0.851
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.118
Final R indices [$I > 2\sigma(I)$]	R1=0.0579, wR2 = 0.1667
R indices (all data)	R1 = 0.0695, wR2=0.1753

Table 2. The important bond distances (Å) 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) #3	2.481(3)

Table 3. The important angles (°) 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) metal 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.

Figure 1. The structure of one-dimensional chain

Figure 2. Packing of the chain in crystal for complex

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 $\chi_M T$ 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 ($4I9/2$) and two uncoupled radicals ($S = 1/2$). As temperature goes down, the value of $\chi_M T$ achieves a minimum of $0.96 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The reason why $\chi_M T$ 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 χ_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).

Figure 3. Plots of $\chi_M T$ vs. T and χ_M^{-1} vs. T for complex

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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