A dinuclear gadolinium complex based on schiff base ligand: structure and magnetic properties

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Abstract. A novel dinuclear dysprosium complex, namely \([\text{Gd}_2 (L)_4 (\text{C}_2\text{H}_3\text{O}_2)_2 (\text{CH}_3\text{OH})_2]\) (1) (L=2-hydroxy-3-methodxybenzaldehyde-5-bromo oxime), was synthesized, structurally and magnetically characterized. Single-crystal X-ray structural analysis reveals that complex 1 is neutral dinuclear complex, in which two Gd (III) ions with nine-coordinated environment are bridged by two phenoxide groups from two Schiff base ligands and four O ions from two molecules of methanoic acid. The magnetic study of complex 1 indicates the slow relaxation of magnetization.

1. Introduction

The study of single-molecule magnets (SMMs) has a booming development since its discovery during 1990s. It has some potential applications in high-density information storage, quantum computing devices and so on [1]. Among all the centre ions, owning to their significant magnetic anisotropy which arising from the large, unquenched orbital angular momentum, lanthanide-ions are widely used to construct SMMs [2]. For example, Tong’s group reported a Dy-based compounds with pronounced magnetic hysteresis loops up to 14 K and the effective energy barrier reached a record of \(U_{\text{eff}} = 1025 \text{ K}\) for relaxation [3]. For the purpose of adjusting the magnetic properties, studies show that the magnetic interaction between centre metals and the alteration of coordination geometry on them are important factors [4]. Moreover, the dinuclear SMMs are idea configurations to study the single-ion effective anisotropic barriers versus the energy barriers which arising from the two interaction metal centers [5].

In order to construct dinuclear SMMs, the choice of ligands are important. Previous study show that Schiff-base ligands are excellent candidates to construct lanthanide-based multinuclear coordination compounds. By carefully modify the terminal group of acylhydrazine derivatives, various of ligand systems has been built. In addition, ligand field will affects the SMM properties of Ln (III) coordination compounds.

In this paper, we choose 2-hydroxy-3-methodxybenzaldehyde-5-bromo oxime as ligand in combination with acetic acid to build a new Gd-based coordination polymer, namely \([\text{Gd}_2 (L)_4 (\text{C}_2\text{H}_3\text{O}_2)_2 (\text{CH}_3\text{OH})_2]\) (1) (L = 2-hydroxy-3-methodxybenzaldehyde-5-bromo oxime). Its synthesis, crystal structure and magnetic property were reported here.
2. Experimental

2.1. Materials and measurements
All reagents and solvents were purchased from Aladdin and used without further purification. The radical ligand 2-hydroxy-3-methoxybenzaldehyde-5-bromo oxime was synthesized according to the literature [6]. Variable temperature magnetic susceptibilities were measured on SQUID MPMSXL-7 magnetometer in the temperature range from 2 K to 300 K. The suitable single crystal of complex 1 was used for X-ray diffraction data collection with a BRUKER SMART 1000 CCD, all using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved primarily by direct methods and refined by the full-matrix least squares method. The computations were performed with the SHELXL-97 program. 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.

2.2. Synthesis of complex 1
Ligand L (0.1 mmol) was dissolved in CH3OH/CH3CN (10 mL/5 mL) followed by the addition of GdCl3·6H2O (0.1 mmol) and triethylamine (0.2 mmol), which gave a clear pale-yellow solution after stirring for 2.5 h. Diethyl ether was allowed to diffuse slowly into this solution at room temperature, and yellow single crystals were obtained in 5 days.

3. Results and discussion

3.1. Crystal structure
The crystal structure of complex 1 is shown in Fig.1 which is crystallized in monoclinic with space group of P21/c. The two Gd ions are bridged by two molecules of acetate ion and two phenoxide groups. The Gd–O and Gd–N distances are in the range of 0.238 9(4) – 0.275 0(4) nm and 0.267 7(3) – 0.272 9(2) nm, respectively. The intramolecular Gd⋯Gd distance is 0.387 7(1) nm and Gd-O-Gd angle of 104.30(5) °.

Figure 1. Crystal structure of complex 1 with thermal ellipsoids drawn at 30% probability. All hydrogen atoms are omitted for clarity.
3.2. Magnetic properties of complex 1

Variable-temperature magnetic susceptibilities of complex 1 were measured from 300 to 2.0 K in an applied field of 1 kOe. As shown in Fig. 2, the χMT value for complex 1 at 300 K is 15.68 cm³ K · mol⁻¹, which is in good agreement with the expected value of 15.76 cm³ K · mol⁻¹ for two uncoupled Gd³⁺ ions (⁸S₇/₂, S = 7/₂). The χMT value is almost stable until the temperature cooling to 35 K and start to decrease rapidly, then reaching a minimum value of 11.05 cm³ K · mol⁻¹ at 3.0 K. This observed different temperature indicates the presence of a weak antiferromagnetic interaction between the Gd³⁺ ions.

![Fig. 2 Temperature dependence of χMT for complex 1. The solid line represents the theoretical values based on the corresponding equation.](image)

To evaluate the coupling parameters, the magnetic data were analyzed by a theoretical expression. The best fit from equation below gives g = 1.99, J = -0.1348 which confirms the weak antiferromagnetic interaction between the Gd ions.

\[
\chi_m = \frac{2Ng^2e^{-\beta\omega}}{kT} \times \\
\left( \exp(J/kT) + 5\exp(3J/kT) + 14\exp(6J/kT) + 30\exp(10J/kT) + 55\exp(15J/kT) + 91\exp(21J/kT) + 140\exp(28J/kT) \\
1 + 3\exp(J/kT) + 5\exp(3J/kT) + 7\exp(6J/kT) + 9\exp(10J/kT) + 11\exp(15J/kT) + 13\exp(21J/kT) + 15\exp(28J/kT) \right)
\]

4. Conclusion

A novel Schiff based-dinuclear Dy complex has been successfully synthesized. Single-crystal X-ray structural analysis reveals that this complex is neutral dinuclear complex, in which two Dy(III) ions with nine-coordinated environment. Its magnetic susceptibilities to an alternating current revealed that this dinuclear Dy complex exhibits slow relaxation of magnetization.

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