A dinuclear dysprosium complex based on schiff base ligand: synthesis, structure and magnetic property

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Abstract. A novel dinuclear dysprosium complex, namely [Dy2 (L)4 (COO)2 (CH3OH)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 Dy(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
Since the discovery of single-molecule magnets (SMMs) during the 1990s, the study of SMMs has a booming development for its potential application 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 $U_{\text{eff}} = 1025$ K for relaxation [3]. Previous studies show that the magnetic interaction between centre metals and the alteration of coordination geometry on them are important factors to adjusting the magnetic properties of lanthanide-based SMMs [4]. In addition, 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].

To construct dinuclear SMMs, the choice of ligands is very important. According to previous study, Schiff-base ligands have been regarded as excellent candidates to construct lanthanide-based multinuclear coordination compounds. By modify the terminal group of acylhydrazine derivatives, various of ligand systems will be built in which ligand field will also affects the SMM properties of Ln (III) coordination compounds.

Herein, we choose 2-hydroxy-3-methodxybenzaldehyde-5-bromo oxime as ligand in combination with methane acid to build a new Dy-based coordination polymer, namely [Dy$_2$ (L)$_4$ (COO)$_2$ (CH$_3$OH)$_2$] (1) (L = 2-hydroxy-3-methodxybenzaldehyde-5-bromo oxime). Its synthesis, crystal structure and magnetic property were reported in this paper.
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 CH$_3$OH/CH$_3$CN (10 mL/5 mL) followed by the addition of DyCl$_3$·6H$_2$O (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 depicted in Fig.1. Complex 1 crystallizes in the space group of $P-1$ in triclinic structure. The two symmetric nine-coordinate Dy$^{III}$ ions are bridged by two phenoxide groups from two schiff base ligands and four O ions from two molecules of methanoic acid with Dy-O phenoxide bond length of 2.368 Å and 2.356 Å, respectively. Then, each Dy$^{III}$ ion is further coordinated with the two N ions from oxime, one O$_{hydroxyl}$ ion, one O$_{methoxyl}$ ion and one O$_{methanol}$ ion. The intramolecular Dy⋯Dy distance is 3.774 Å with Dy-O-Dy angle of 106.055(4)°.
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 $\chi_M T$ value of 28.62 cm$^3$ K·mol$^{-1}$ is close to the ideal value of 28.34 cm$^3$ K·mol$^{-1}$ for two non-interacting Dy$^{III}$ ions ($^{6}H_{15/2}$, $g = 4/3$). While cooling, the $\chi_M T$ value decrease gradually from 300 K to 50 K, then decrease quickly and reaching a value of 6.9 cm$^3$ K·mol$^{-1}$ at 2 K. This phenomenon at high temperature results from the depopulation of the excited Stark sublevels. However, at low temperature, the decrease behaviour mainly results from intramolecular antiferromagnetic interaction between Dy (III) ions.

In order to investigate the dynamic magnetic properties of complex 1, the temperature frequency dependencies of magnetic susceptibility measurements under alternating current were measured in the range of 200-1000 Hz. As shown in Figure 3, complex 1 exhibits a frequency dependent character in the in-phase signal ($\chi'$) and out-of-phase signal ($\chi''$), indicating the slow relaxation of magnetization.
Figure 4. In-phase (left) and out-of-phase (right) ac susceptibilities of complex 1 at different frequencies (from 200 to 1000 Hz) under zero applied field.

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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