Syntheses, crystal structures and magnetic properties of sandglass Dy_9^{III} and irregular tetrahedron Dy_4^{III} complexes

Hui-Sheng Wang *, Qiao-Qiao Long, Cheng-Ling Yin, Zi-Wei Xu, Zhi-Quan Pan

School of Chemistry and Environmental Engineering, Key Laboratory of Green Chemical Process of Ministry of Education, Key Laboratory of Novel Reactor and Green Chemical Technology of Hubei Province, Wuhan Institute of Technology, Wuhan 430074, PR China

ABSTRACT

The synthesis, crystal structures, and magnetic properties of a nonanuclear dysprosium complex $[Dy_9(\mu_3\text{-}OH)_8(\mu_4\text{-}OH)_2(N_3)_8\{(py)_2C(OCH_3)O\}_8](OH)\cdot 4H_2O$ (**1**, $(py)_2C(OCH_3)OH$ = the hemiacetal form of di-2-pyridyl ketone) and a tetranuclear dysprosium complex $[Dy_4(\mu_4\text{-}O)(\mu\text{-}N_3)_2(\mu\text{-}OCH_3)_2(L)_4](OH)_2\cdot 3.5CH_3OH$ (**2**, HL = 2-(benzothiazol-2-yl-hydrazonomethyl)-6-methoxyphenol) have been prepared and structural characterization. Nine Dy^{III} ions in **1** form a sandglass with the eight Dy^{III} atoms at the apexes and one Dy^{III} ion located at the center of a square antiprism formed by eight Dy^{III} ions, while four Dy^{III} ions in **2** form an irregular tetrahedron. Complexes **1** and **2** have been investigated by direct current (dc) and alternating current (ac) susceptibility measurements. The ac susceptibility studies revealed that complexes **1** and **2** exhibit slow magnetic relaxation. Moreover, complex **2** shows two-step thermal magnetic relaxation with their energy barriers of about 15 K and 2.68 K, respectively. The orientations of the magnetic anisotropy of Dy^{III} ions in **1** and **2** were also estimated by electrostatic calculations.

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1. Introduction

Single-molecule magnets (SMMs) are a focused material in recent years, mainly due to their potential applications for memory storage devices, molecular spintronics and quantum computation [1]. SMMs are discrete molecular complexes which possess slow relaxation after removing external magnetic field and the origin of molecular magnetism in SMMs is energy barrier (*U*) of the magnetization reversals between 'spin up' state and 'spin down' state [2,3]. For the 3d transition metal SMMs complexes, the energy barrier can be improved by increasing the value of spin ground state (*S*) and Ising-type magnetic anisotropy (negative zero-field splitting parameter, *D*) [4]. However, in 2008, Ruiz et al. have drawn a conclusion that large magnetic anisotropy is not favored by a high spin state of the ground state through theoretical study of two Mn_6 complexes [5]. Indeed, in some high-nuclear Mn complexes, the spin ground state can be maximized through ferromagnetic couplings between paramagnetic ions within these complexes, however, their magnetic anisotropy is very low (close to zero), which may be due to mutual perpendicular for the Jahn–Teller axes of Mn^{III} ions within these complexes [6]. Therefore, synthesis of SMMs with a large magnetic anisotropy

may be another option [7,8]. Ln-ions are a good candidate to meet this demand, because it have no quenching of the orbital angular momentum in the crystal field, which result in the strong spin orbit coupling interactions and further make 4f ions possess significant magnetic anisotropy [9–12].

In many of the lanthanide metal ions, dysprosium is considered to be the most suitable candidate in the study of 3d-4f and 4f SMMs [13,14]. The reason is that Dy^{III} possesses high anisotropy of the spin–orbit coupled Kramers doublet ground state, and it have a large separation between the doublet ground state and the first excited state or the higher excited states, which leads to the slow spin relaxation phenomenon [15,16]. Up to date, many Dy^{III} SMMs complexes with different structural topologies, such as Dy_3^{III}, Dy_6^{III}, Dy_8^{III}, Dy_{10}^{III}, Dy_{11}^{III}, Dy_{12}^{III} et al. [17–22], have been obtained. However, due to the weak magnetic coupling interactions and the obviously quantum tunneling effect, the challenge of improving energy barrier remains [23,24].

Quantum tunneling of magnetization (QTM) is resulted from the mixing of $\pm M_J$ level *via* hyperfine coupling, dipolar spin–spin interactions, or transverse anisotropy (*E*) [25a]. The latter two factors can be minimized by improving the symmetry of coordination geometry of a Kramers ion [25b]. The Dy^{III} ions with high symmetries like $C_{\infty v}$, $D_{\infty h}$, S_8 (I_4), D_{4d}, D_{5h} and D_{6d} can decrease QTM of the SMMs complexes [25c]. Our group has recently been investigating the syntheses, crystal structures and magnetic

properties of polynuclear 3d and 3d-4f complexes containing two organic ligands to regulate the structural topologies of metal ions [26]. In this paper, we will turn to synthesize Dy^{III} complexes containing two organic ligands with different symmetries and coordination modes, to regulate the topologies of Dy complexes and to make Dy^{III} within complexes possess the high symmetries of coordination geometries as stated above. Reaction between Dy(NO$_3$)$_3$·5H$_2$O, di-2-pyridyl ketone (dpk), NaN$_3$ and 2-(Hydroxymethyl)pyridine (Hhmp) or HL ligands in the methanol solution containing triethylamine, obtained the crystals of [Dy$_9$(μ_3-OH)$_8$-(μ_4-OH)$_2$(N$_3$)$_8${(py)$_2$C(OCH$_3$)O}$_8$](OH)·4H$_2$O (**1**, (py)$_2$C(OCH$_3$)OH = the hemiacetal form of dpk) or [Dy$_4$(μ_4-O)(μ-N$_3$)$_2$(μ-OCH$_3$)$_2$(L)$_4$](OH)$_2$·3.5CH$_3$OH (**2**, HL = 2-(benzothiazol-2-yl-hydrazonomethyl)-6-methoxyphenol). It should be noted that complexes **1** and **2** contain only one kind of organic ligand. The reason may be that the coordination ability of dpk is greater than that of Hhmp in compound **1**, while the coordination ability of HL is greater than dpk in compound **2**, so that resulting in only one organic ligand coordinated to the metal in the process of reaction. Certainly, one organic ligand with large steric hindrance is not easy to coordinate with metal ions in the formation of **1** and **2**. Here, we describe the synthesis, crystal structures and magnetic properties of **1** and **2**.

2. Experimental

2.1. Materials and physical methods

All synthetic procedures were completed under aerobic conditions, and all of the reagents and the chemicals were obtained through commercial sources and were used without further purification. The 2-(benzothiazol-2-yl-hydrazonomethyl)-6-methoxyphenol ligand (HL, Scheme 1a) was prepared by the already reported method [27]. Caution! Azide salts is potentially explosive and should be used in small quantities and with utmost care at all times.

2.2. Synthesis of [Dy$_9$(μ_3-OH)$_8$(μ_4-OH)$_2$(N$_3$)$_8${(py)$_2$C(OCH$_3$)O}$_8$](OH)·4H$_2$O (**1**)

A mixture of Dy(NO$_3$)$_3$·5H$_2$O (0.0686 g, 0.15 mmol), di-2-pyridyl ketone (0.0276 g, 0.15 mmol), 2-(Hydroxymethyl) pyridine (0.0164 g, 0.15 mmol), NaN$_3$ (0.0098 g, 0.15 mmol) and triethylamine (0.0455 g, 0.45 mmol) was stirred in methanol (MeOH, 30 mL) for 2 h, resulting in a colorless slightly turbid solution, then the solution was filtered. Colorless crystals were collected by filtration after slow evaporation of the resulting solution for about 20 days. Yield: 15 mg (about 23% based on Dy salt). Elemental analysis (%), calcd for C$_{96}$H$_{107}$Dy$_9$N$_{40}$O$_{31}$ (M_r = 3779.72): C 30.51, H 2.85, N 14.82; Found: C 30.47, H 2.86, N 14.76. IR data (KBr, v/cm^{-1}, s, m and w stand for strong, medium and weak, respectively): 3451 (s), 2954(w), 2821(w), 2075(s), 1601(m), 1571(w), 1508(m), 1472 (m), 1437(s), 1384(s), 1288(m), 1260(m), 1228(m), 1157(w), 1108(s), 1067(s), 1013(m), 987(m), 785(s), 683(s), 634(m), 489(m).

2.3. Synthesis of [Dy$_4$(μ_4-O)(μ-N$_3$)$_2$(μ-OCH$_3$)$_2$(L)$_4$](OH)$_2$·3.5CH$_3$OH (**2**)

A mixture of Dy(NO$_3$)$_3$·5H$_2$O (0.0343 g, 0.075 mmol), di-2-pyridyl ketone (0.0138 g, 0.075 mmol), HL ligand (0.0112 g, 0.0375 mmol), NaN$_3$ (0.0060 g, 0.092 mmol) and triethylamine (0.0228 g, 0.225 mmol) was stirred in methanol (MeOH, 20 mL) for 2 h, resulting in a bright yellow solution, then the resulting solution was filtered. Yellow crystals were collected by filtration after slow evaporation of the resulting solution for about 15 days. Yield: 7 mg (about 17% based on Dy salt). Elemental analysis (%), calcd for C$_{62}$H$_{56}$Dy$_4$N$_{18}$O$_{13}$S$_4$ (M_r = 2039.48, 3.5 solvent CH$_3$OH molecules

were free): C 36.51, H 2.77, N 12.36; Found: C 36.55, H 2.78, N 12.39. IR data (KBr, v/cm^{-1}, s, m and w stand for strong, medium and weak, respectively): 3427(s), 2939(w), 2063(s), 1640(s), 1606 (s), 1548(m), 1458(s), 1405(w), 1300(w), 1262(w), 1242(m), 1220 (s), 1168(w), 1065(m), 1012(w), 965(m), 848(m), 783(w), 740(m), 634(w), 604(w), 509(w), 473(w), 444(m).

2.4. Physical measurements

Fourier transform infrared spectra (IR) were taken with a VECTOR 22 spectrometer at room temperature using KBr pellets in the range of 4000–400 cm^{-1}. Elemental analysis of C, H, N was performed using an Elementary Vario Perkin-Elmer 240C analyzer. The magnetic properties of polycrystalline samples of **1**–**2** were performed with a Quantum Design MPMS-XL7 superconducting quantum interference device (SQUID) magnetometer. The direct current (dc) magnetic susceptibilities were collected in the 2–300 K temperature range in a dc magnetic field of 1000 Oe and the alternating-current (ac) measurements were performed in a zero-applied dc field or in a 1000 Oe for **1** (500 Oe for **2**) dc field with a 5.0 Oe ac field oscillating at frequencies in the range of 1–999 Hz and in the temperature range of 2.0–15 K. The diamagnetic corrections for **1**–**2** were estimated using Pascal's constants.

2.5. X-ray crystallographic studies

Single-crystal data for complexes **1** and **2** were collected at 173 K on a Bruker Smart CCD diffractometer with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) by ω-scan mode. The collected data were reduced using the software package SAINT [28], and semi-empirical absorption correction was applied to the intensity data using the SADABS program [29]. The structure of **1** and **2** were solved using direct methods, and all non-hydrogen atoms were refined anisotropically by least squares on F^2 using the SHELXT-2014 program [30]. Hydrogen atoms were placed in calculated positions and refined isotropically using the riding model. Some solvent molecules in compound **1** and **2** cannot be properly modeled, so the contributions were subtracted by the SQUEEZE command as implemented in PLATON [31]. Unit cell data and structure refinement details are listed in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Tables S1 and S2, respectively.

3. Results and discussion

3.1. Synthesis

Previous studies have shown that if two different ligands are selected to react with magnetic spin carrier salts, novel complexes containing mixed organic ligands can be obtained. Moreover, the change of the number of metal nuclearity and coordination geometry of rare earth ions affect the magnetic anisotropy and the energy barriers. According to the rules of the hard soft acid base (HSAB) theory, the hydroxyl/phenoxido O atoms and pyridyl N atoms on the selected 2-(benzothiazol-2-yl-hydrazonomethyl)-6-methoxyphenol (HL), 2-(Hydroxymethyl)pyridine (Hhmp) and hemiacetal form of di-2-pyridyl ketone (dpk) (Scheme 1) belong to hard base, and Dy^{III} ion belongs to hard acid. Therefore, dpk and Hhmp (or dpk and HL) may be simultaneously coordinated with Dy^{III} ions to form Dy complexes with mixed organic ligands. In this work, we selected Dy(NO$_3$)$_3$ 5H$_2$O, di-2-pyridyl ketone, NaN$_3$ reacting with Hhmp or HL ligands in the presence of MeOH containing triethylamine. However, the obtained Dy$_9$ (**1**) and Dy$_4$ (**2**) contain only one organic ligand.