



Short communication

Slow magnetic relaxation in a two-dimensional dysprosium(III) coordination polymer

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ARTICLE INFO

Article history:

Received 13 April 2016

Received in revised form 11 May 2016

Accepted 15 May 2016

Available online 19 May 2016

Keywords:

Dysprosium

Two-dimensional coordination polymer

Slow magnetic relaxation

ABSTRACT

A new two-dimensional (2D) dysprosium(III) coordination polymer, e.g. $[\text{Dy}(\text{HL})(\text{NO}_3)_2(\text{H}_2\text{O})]_n$ (**1**, $\text{H}_2\text{L} = 4-[(2\text{-hydroxy-3-methoxyphenyl})\text{methylidene}]\text{amino}]\text{benzoic acid}$), has been solvothermally synthesized and structurally characterized using single-crystal X-ray diffraction. The dysprosium ions in complex **1** display the capped trigonal prism geometry and are connected with each other through o-vanillin and carboxyl groups, generating an interesting 2D structure with a Shubnikov topological symbol of $\{3^2.4.3.4\}$ (tts). Magnetic investigations indicate that the coordination polymer exhibits slow magnetic relaxation.

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In the past two decades, the study of single molecule magnets (SMMs), which could exhibit slow magnetic relaxation at molecule level, is a highly active research topic in the fields of chemistry, physics and materials science [1]. Such nanomagnetic materials permitted the observation of fascinating quantum phenomenon and may potentially be utilized for high-density magnetic storage as well as quantum computer and spintronics [2]. Recently, it is noted that the strong anisotropy which is mainly determined by the strength of spin-orbit coupling, plays a vital role in creating SMMs with high anisotropic barriers (U_{eff}) [3]. In this regard, significant attention has been paid to the synthesis of molecules containing lanthanide ions [4], especially the Dy^{III} ions, mainly because of the existence of large magnetic moments and remarkable magnetic anisotropy in the Dy^{III} ions [5]. To date, a flood of Dy-based SMMs (DySMMs) have been reported in the literature, and most of them are monometallic or polynuclear systems [6], whereas reports on two-dimensional (2D) dysprosium(III) coordination polymers (DyCPs) are limited. Despite this, several originally studied 2D DyCPs show obvious ferromagnetic interactions and possess typical SMM behaviours [7], representing a promising avenue towards new generation of molecular magnetic materials. In view of these aspects, it is of primary importance to design and study more 2D DyCPs with novel structures and magnetic couplings, with the goal of improving our knowledge on magnetostructural relationships in these complexes. Herein, we describe the synthesis, crystal structure and magnetic properties of a new 2D DyCPs, $[\text{Dy}(\text{HL})(\text{NO}_3)_2(\text{H}_2\text{O})]_n$ (**1**) [8], which shows an interesting structure and slow relaxation of the magnetization.

Complex **1** was obtained by the reaction of H_2L and $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in ethanol via solvothermal synthesis and studied by simultaneous

thermogravimetric-differential thermal analysis (TG-DTA) (Fig. S2). The mass loss below 135 °C is 8.51%, which could be attributed to the remaining ethanol molecules coming from the mother liquor. The material continues to lose a further 3.12% mass out to 295 °C, corresponding to the loss of one water molecule bound to the metal center (calc. 3.15%). The decomposition nearly complete around 1000 °C with 33.23% mass remaining, presumably as Dy_2O_3 (calc. 34.86%). The high phase purity of the bulk samples is further confirmed by the PXRD study (Fig. S3).

Single crystal X-ray crystallographic results reveal that complex **1** is monoclinic crystal system, space group $P2_1/c$ with $Z = 4$. The center Dy^{III} ion (Dy1) displays $\{3^2.4^3.5^4\}$ point symbol and coordinates with three HL^- anions, two nitrate ions and one water molecule into a $\{\text{DyO}_9\}$ distorted capped square antiprism geometry (Fig. S4, S5). There are two separated bidentate groups coexisted in the HL^- anions, which are the o-vanillin group (O1, O2) in a $\mu_1:\eta^1:\eta^1$ fashion with the chelating mode, and the carboxyl group (O3, O4) in a $\mu_2:\eta^1:\eta^1$ fashion as a bismonodentate bridge, whereas the nitrogen atom remains uncoordinated. The Dy–O bond distance for $\mu_2:\eta^1:\eta^1$ coordination mode 2.282(9) to 2.238(8) Å, are shorter than those for $\mu_1:\eta^1:\eta^1$ coordination mode 2.341(10) to 2.564(11) Å, implying stronger bonds (Table S2). As a result, two adjoining Dy atoms are connected by two o-vanillin groups and two carboxyl groups from four HL^- anions forming a dinuclear unit (Fig. 1, left). The distance between the two Dy^{III} centers is 5.3721(10) Å, while the $\text{Dy}^{\text{III}}-\mu_2-\text{O}^{2-}-\text{Dy}^{\text{III}}$ bond angle is 89.355(3). It is believed that when the Dy–O–Dy angle is larger than 110°, ferromagnetic interactions are usually favorable [9]. Therefore, an antiferromagnetic interaction may exist in complex **1** (below 110°). The neighbouring dinuclear units continuously link to each other through four HL^- ligands generating a highly ordered 2D network with two layer structure. The whole network can be simplified as 3-connected net with a Shubnikov topological symbol of $\{3^2.4.3.4\}$ (tts) (Fig. 1, right). There is presence of

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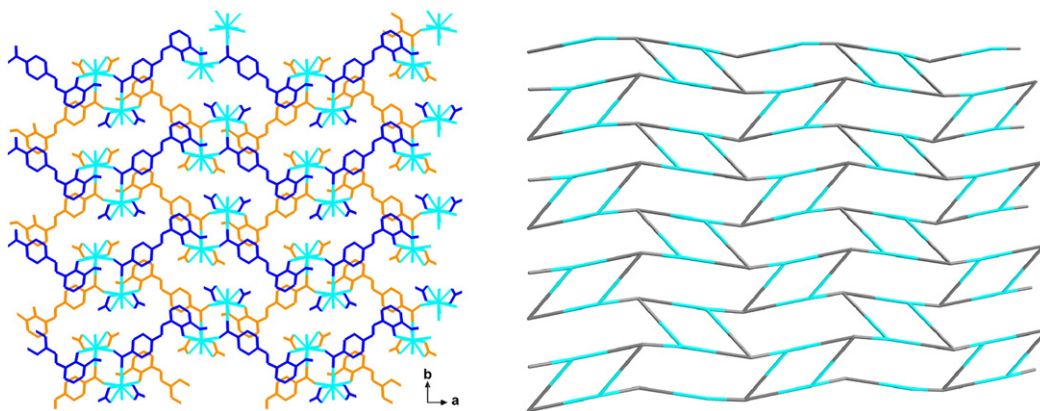


Fig. 1. Perspective view of the two dimensional structure of complex **1** (left) and the topological view of the 2D structure along *c* axis (right). Turquoise, Dy; H atoms are omitted.

intermolecular O–H···O hydrogen bond between the nitrate oxygen atoms O6, O7 and the symmetry equivalent water oxygen atom O11 (Fig. S6). In addition, π – π stacking interactions also exist between the HL[−] ligands within the two layers structure (Fig. S7). As a result, these two types of interactions may play complementary roles for stabilizing the network structure. The distances between the neighbouring dinuclear units are as long as 1.392 nm and 1.083 nm (Fig. S8), respectively, which means that magnetic exchange between the dinuclear units can be ignored [7a].

The dc magnetic susceptibility studies of complex **1** were carried out in an applied magnetic field of 1000 Oe in the temperature range of 300–2 K. The χ_m^{-1} and $\chi_m T$ vs. *T* plots for **1** are shown in Fig. 2. The observed $\chi_m T$ value at 300 K is determined to be 14.58 emu mol^{−1} K, which is slightly higher than the expected value for each dysprosium ion ($J = 15/2$, $g_J = 4/3$, $\chi_m T = 14.17$ emu mol^{−1} K). Above 100 K, the $\chi_m T$ value gradually decreases upon cooling, and the tendency is more obvious above 50 K. Then it drops sharply to reach a minimum of 11.15 emu mol^{−1} K at 2 K. The fast decreasing in $\chi_m T$ is likely due to the progressive depopulation of Dy^{III} excited Stark sublevels, crystal-field effect of the free Dy^{III} ions and/or possible exchange interaction between the metal ions [10]. The Curie–Weiss analysis of the magnetic susceptibility data over the temperature ranges 2–300 K results in the Curie constant $C = 14.75$ emu mol^{−1} K and the Weiss constant $\theta = -3.92$ K for **1**. As compared with other reported 2D dysprosium (III) compounds, in which the central ions occupy high symmetry coordination geometry and show intramolecular ferromagnetic interactions [7], the distorted capped square antiprism geometry of Dy^{III} ions in complex **1** may be unfavorable for the ferromagnetic coupling between the Dy^{III} ions.

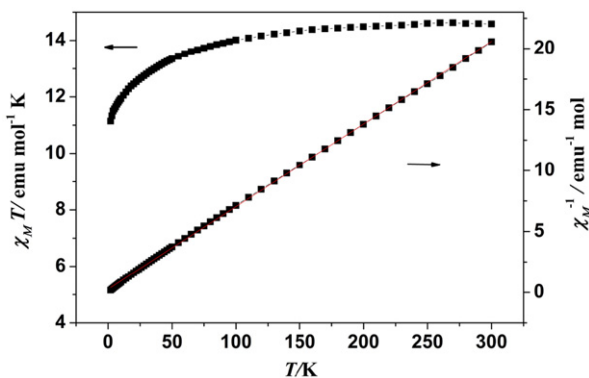


Fig. 2. Temperature dependence of $\chi_m T$ products under a dc field of 1000 Oe at 2–300 K. The red solid line corresponds to the fitting of Curie–Weiss law.

The variation of the magnetization *M* with the applied magnetic field *H* was investigated for **1** in the range of 0–70 kOe below 8.0 K (Fig. 3). *M* increases rapidly at low field and reaches a value of 5.37 μ_B for **1** at 2 K and 70 kOe. The value is lower than the theoretical saturated value of 10 μ_B for one independent Dy^{III} ion, but close to uncorrelated Dy^{III} ions' magnetic moments (5.23 μ_B), which could be attributed to the ligand-field-induced splitting of the Stark level as well as magnetic anisotropy [11]. Furthermore, both the lack of saturation of the *M* vs *H* data and the nonsuperimposition of the *M* vs *H*/*T* data at 2.0–8.0 K confirm the presence of anisotropy and/or low-lying excited states [12], which is expected for compound containing Dy^{III} ions.

The magnetization dynamics of complex **1** were investigated from the ac susceptibility measurements in a 2.0 Oe oscillating field at different frequencies (Fig. 4, left). Apparently, an obvious frequency dependent below 10 K is detected for **1**, indicating the onset of slow magnetic relaxation behaviour, which could be expected for a SMM. However, no maximum of χ''_m is observed, which may be due to fast zero-field quantum tunneling. Therefore, a 2000 Oe dc field was applied to suppress any possible tunneling effects. As it could be seen (Fig. 4, right), the $\chi''_m(T)$ plot shows a broad shoulder between 4 and 8 K in the range 500–1000 Hz with still no resolvable maximum observed, which further confirms the occurrence of quantum tunneling [13]. As for the Dy-containing compounds, it has been proved that the highly symmetric crystal-field environments play important role on its excellent SMM behaviours. Therefore, the presence of fast quantum tunneling relaxation in complex **1** should originate from the low symmetry coordination geometry of the local Dy site and weak intramolecular interactions between the Dy^{III} ions [14].

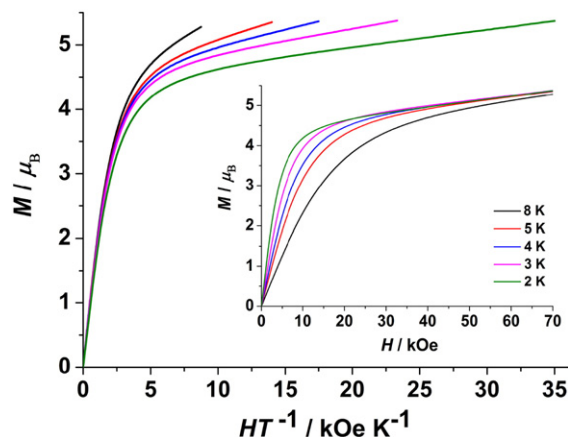


Fig. 3. Plots of the reduced magnetization *M* versus *H*/*T* for **1** in the field range 0–70 kOe and temperature range 2–8 K. Inset: Field dependence of the magnetization for **1**.

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