



Short communication

## Slow magnetic relaxation in a carboxylate-bridged one dimensional dysprosium complex

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## ABSTRACT

A new carboxylate-bridged dysprosium complex, e.g.  $[\text{Dy}_2(\text{PAA})_6]_n$  (**1**,  $\text{PAA}^- = 4\text{-aminobenzoic acid anion}$ ), was synthesized under solvothermal conditions and fully characterized. Single crystal X-ray crystallography analysis reveals that complex **1** consists of linear chains built up by  $\text{Dy}_2(\text{PAA})_6$  units and bridged only by carboxylate groups. The magnetic studies indicate that the coordination polymer exhibits slow magnetic relaxation, suggesting single molecule magnet behavior.

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Single molecule magnets (SMMs) have received considerable attention due to their promising applications in high-density information storage, quantum computing and molecular spintronics [1]. There are two essential requirements have to be met to obtain an SMM, including large negative axial magnetic anisotropy ( $D$ ) and high spin values ( $S$ ), which eventually leading to an anisotropic energy barrier ( $U_{\text{eff}}$ ) to reversal of the molecular magnetization [2]. Lanthanide elements, especially for the  $\text{Dy}^{\text{III}}$  ion, have been identified to be extremely useful for constructing new SMMs, benefiting from its strong uniaxial magnetic anisotropy and large magnetic moments [3]. Up to now, a library of dysprosium ( $\text{Dy}$ )-based SMMs with polynuclear structure has been reported [4]. However, the highest blocking temperature for an SMM is limited below 14 K [5], which led to slow relaxation of magnetization only at liquid helium temperatures, made the major obstacle to realize the applications of SMMs [6]. Furthermore, studies on magnetic properties of lanthanide chains, especially for one-dimensional  $\text{Dy}^{\text{III}}$  chains are rather limited [7], which is mainly because of the weak magnetic couplings between  $\text{Ln}^{3+}$  ions. Two cases of homospin  $\text{Dy}^{\text{III}}$  chains with similar ligands, 4-nitrobenzoate and 2-methylbenzoic acid [8,9], showed different chain structures and magnetic properties, suggesting the importance of local ligand field of the central ion in a 1D system, which is crucial to the magnetic anisotropy of the central ion and the slow relaxation behavior [10]. In view of these aspects, synthesizing more 1D  $\text{Dy}$ -based system with different structures and magnetic coupling is of fundamental importance to enhance the knowledge of the magnetic properties of Ln-based chains. Herein, we report a  $\text{Dy}$ -based

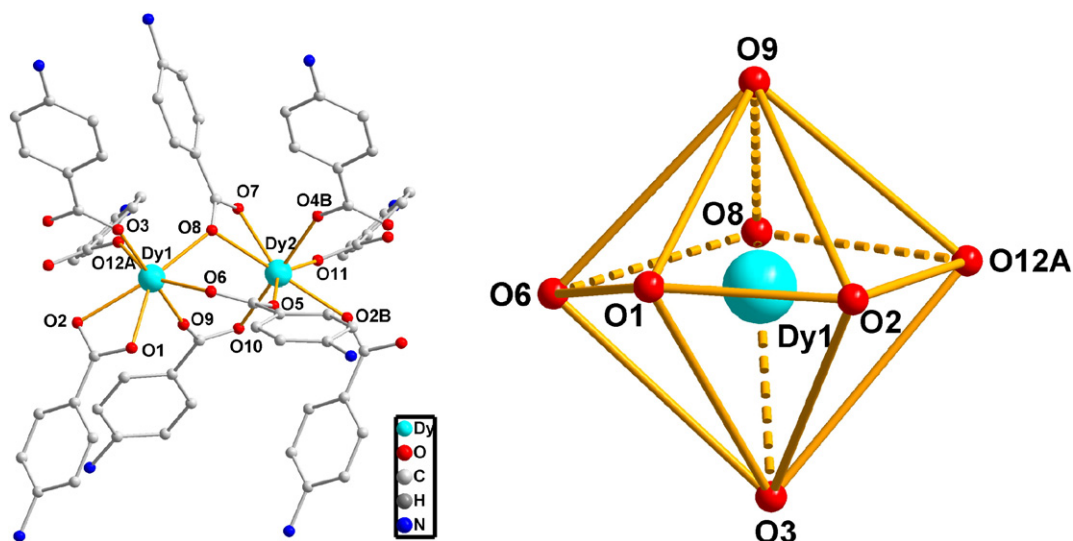
1D chain assembled using 4-aminobenzoic acid (HPAA) as ligand [11]. The compound shows interesting structure and slow relaxation of the magnetization behavior.

Via solvothermal synthesis (75 °C), the self-assembly of HPAA and  $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in ethanol in the presence of NaOH generated compound **1**. In the IR spectrum of the compound, the absence of characteristic absorption of  $\nu_{\text{as}}(\text{COOH})$  near  $1670\text{ cm}^{-1}$  indicates that 4-aminobenzoic acid is completely deprotonated [12]. The  $\nu_{\text{as}}(\text{COO}^-)$  vibration of the carboxylate group occurred at  $1605$  and  $1554\text{ cm}^{-1}$ , while the  $\nu_{\text{s}}(\text{COO}^-)$  occurred at  $1396\text{ cm}^{-1}$ , evidence the presence of both chelating bidentate and bis-monodentate modes of the ligand (Fig. S1.).

Single crystal X-ray crystallographic analysis reveals that complex **1** crystallizes in the triclinic,  $P_{-1}$  space group with  $Z = 4$ . The asymmetrical unit contains two crystallographically independent  $\text{Dy}^{\text{III}}$  ions and six  $\text{PAA}^-$  anions (Fig. 1). The  $\text{Dy1}$  and  $\text{Dy2}$  centers are almost totally equivalent with seven-coordination geometry and have only slight perturbation in bond lengths and angles (Table S2, S3). Each central ion locates in a distorted pentagonal bipyramid geometry completed by oxygen atoms from six  $\text{PAA}^-$  ligands only, whereas the nitrogen atoms remaining uncoordinated. The adjacent two  $\text{Dy}^{\text{III}}$  ions are connected by three carboxylate groups of the  $\text{PAA}^-$  ligands, in which one group in a  $\mu_2:\eta^1:\eta^2$  fashion while the other two in a  $\mu_2:\eta^1:\eta^1$  fashion (Fig. 2, left). The  $\text{Dy}-\text{O}$  bond lengths are in the range of  $2.216(6)$ – $2.519(4)$  and  $2.249(5)$ – $2.523(4)$  Å for the  $\text{Dy1}$  and  $\text{Dy2}$  centers, respectively, comparable to those of previously reported dysprosium-oxygen complexes [13]. It is worth noting that the  $\text{Dy}-\text{O}$  bond distance ( $2.216(6)$  to  $2.298(4)$  Å) for  $\mu_2:\eta^1:\eta^1$  coordination mode is shorter than those for  $\mu_2:\eta^1:\eta^2$  coordination mode ( $2.332(4)$  to  $2.523(4)$  Å), implying stronger

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**Fig. 1.** Crystal structure of complex **1** (left) and coordination polyhedron of Dy<sup>III</sup> ion (right) (all hydrogen atoms are omitted for clarity). Symmetry code: #1: 1 + X, +Y, +Z; #2: -1 + X, +Y, +Z.

bonds. The O–Dy–O bond angles range from 52.60(15) to 154.84(16)° while the two Dy<sup>III</sup>–μ<sub>2</sub>-O<sup>2-</sup>-Dy<sup>III</sup> bond angles are 113.67(17) and 116.57(17)° (Table S3). Along *a* direction, as shown in Fig. 2, the neighboring asymmetrical units are further connected by three carboxylate groups to form a 1D infinite chain with a Dy–Dy–Dy angle of 148.269(12)° (Fig. 2, right). The shortest intrachain Dy⋯Dy contacts are 4.066(1) Å, which is shorter than other reported 1D Dy-based chains (4.2 to 11.9 Å) [7,9]. Finally, a 3D supermolecular framework was formed by intermolecular hydrogen bond interactions (Fig. S2). The shortest interchain Dy⋯Dy contacts are 10.7347(27) Å and 11.6273(26) Å for Dy1⋯Dy1 and Dy2⋯Dy2, respectively.

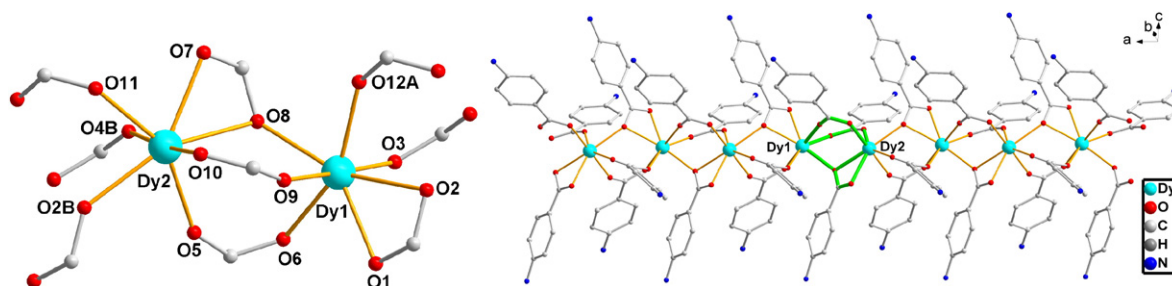
TG studies at 25–1000 °C show that the complex has good thermo-stability and starts to decompose after 400 °C (Fig. S3). The high phase purity of the bulk samples is further confirmed by the PXRD study (Fig. S4).

The temperature dependence of the static field magnetic susceptibility for the complex is collected in the temperature range of 2 to 300 K at 1000 Oe. The plots of  $\chi_m^{-1}$  and  $\chi_m T$  vs. *T* for **1** are shown in Fig. 3. At 300 K, the  $\chi_m T$  value is determined to be 29.45 emu mol<sup>-1</sup> K, which is corresponding to the expected value of 28.34 emu mol<sup>-1</sup> K for two isolated dysprosium ( $J = 15/2$ ,  $g_J = 4/3$ ,  $\chi_m T = 14.17$  emu mol<sup>-1</sup> K). Above 50 K, the  $\chi_m T$  value gradually decreases upon cooling, and the tendency is more obvious above 5.5 K. Then the  $\chi_m T$  curve shows a fast dropping below 5.5 K, and reaches a minimum of 21.21 emu mol<sup>-1</sup> K at 2 K. Such a sharp decrease at low temperature could be attributed to weak intramolecular antiferromagnetic interactions between the spin

carriers and/or the thermal depopulation of the Stark sublevels of the Dy<sup>III</sup> ions [14]. The Curie–Weiss analysis of the magnetic susceptibility data over the temperature ranges 2–300 K gives the Curie constant (*C*) of 29.82 emu mol<sup>-1</sup> K and the Weiss constant ( $\theta$ ) of -3.82 K for **1**. The small negative  $\theta$  value is presumably caused by the antiferromagnetic interaction and/or the crystal-field effect of the free Dy<sup>III</sup> ion [15].

The variation of the magnetization (*M*) with the applied magnetic field (*H*) was investigated for **1** in the range of 0–70 kOe at 2.0 K (Fig. 4). *M* increases rapidly at low field and then grows slowly without complete saturation up to 70 kOe. Its magnetization values (13.21N $\beta$ ) at 70 kOe are lower than the theoretical saturated value of 20N $\beta$  anticipated for two independent Dy<sup>III</sup> ions, which can be attributed to the ligand-field-induced splitting of the Stark level as well as magnetic anisotropy [16]. Furthermore, the plots of *M* vs. *H*/*T* at 2.0–10.0 K show non-superimposed magnetization behavior for complex **1**, confirming the presence of anisotropy and/or low-lying excited states [17], as expected for compound containing Dy<sup>III</sup> ions.

The temperature dependence of alternating-current (ac) magnetic susceptibilities for complex **1** was measured under zero applied dc field and an AC field of 3 Oe at the indicated frequencies given in Fig. 5 (as the plots of  $\chi'_m$  vs. *T* and  $\chi''_m$  vs. *T*). Apparently, the complex **1** shows unnegligible out-of-phase signals. The frequency dependence “tails” of the out-of-phase susceptibility were displayed below 12 K, indicating the slow magnetization relaxation of an SMM with a small energy barrier for magnetization reversal. Such magnetic behavior most likely derives from predominant single-ion effects of individual



**Fig. 2.** Representations of the dinuclear unit of complex **1** (left) and view of the 1D chain structure along *a* axis (right).

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