Original article

Stepwise assembly of heterometallic 3d-4f chain exhibiting slow magnetic relaxation

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ABSTRACT

The self-assembly of polyalcohol ligand 1,1,1-tris(hydroxymethyl)ethane with $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}_3\text{O-Bzo-tBu}$ precursor in the presence of triethylamine step-by-step generated a heterometallic 3d-4f chain. Magnetic investigation of the complex indicates typical slow relaxation of the magnetization at low temperature.

Keywords:

3d-4f

Chain

Stepwise assembly

Slow magnetic relaxation

1. Introduction

Since the observation of slow magnetic relaxation in a cobalt(II) radical alternating chain opened the door to single chain magnets (SCMs) [1], this interesting field has gained considerable attention from chemists and physicists and has been rapidly expanding, owing to their potential applications in high-density information storage, quantum computation, and molecular spintronic [2-5]. Inspiring progress have been made in the field of SCMs with the development of crystal engineering and molecule-based materials, and some predesigned or existing properties and functions could be achieved or mediated at the molecular level [6-7]. To construct SCMs, two basic respects need to be considered: strong uniaxial Ising-type anisotropy, strong intrachain and weak interchain magnetic interaction. According to the requirements, Gao *et al.* [8] summarized three effective strategies to the fabrication of SCMs, ferromagnetic (FO), ferrimagnetic (FI), and weak ferromagnetic (WF) approaches. However, the rational design of such molecular materials is still a challenging task for researchers due to the difficulties in both structural and magnetic controls.

Hitherto, current research mainly utilizes two effective approaches to build SCMs. The most common approach is serendipitous assembly between metal ions with large single-ion anisotropy such as Mn(III), Co(II), Fe(II) and Ln(III) ions [8-11] and suitable ligands that could efficiently mediate intrachain exchange interactions so as to get simultaneously isolate the chains to avoid interchain exchange interactions [12-14]. Although it is not easy to foresee the concrete bonding modes of the resultant products, the approach have been successfully utilized in many related systems. Parallel to the serendipitous assembly, step-by-step assembly has also been well used to obtain the desired products, especially the assembly of pre-existing magnetic units offering the opportunities of targeted synthesis. The feasibility of such two approaches to create SCMs has been well verified in literatures [15].

We have sought to explore the synthetic methodology toward fabricating new SCMs. For example, SCM-like behavior was observed in a unique substituted 3D Co(II)-formate framework with serendipitous assembly approach [2]. Because of the isolation of isonicotinic and the strong anisotropy of spin-canting, the 1D WF chains exhibit slow magnetic relaxations, adding a new member of SCM based on the WF chains. A 2D coordination polymer displaying SCM-like behavior has also been constructed via serendipitous assembly approach [16]. Because the long interchain spacer 1,4-bis(imidazol-1-yl) benzene prevents the magnetic ordering, the FO cobalt chains bridged by μ_2 -1, 1-azido display slow relaxation of magnetization, providing a new case of SCM based on the F chains. As our continuous studies on the synthesis and magnetic investigation of SCMs, in this work we report that the step-by-step assembly of $[\text{Cr}_3\text{O}(\text{Bzo-t-Bu})_6(\text{H}_2\text{O})_3]\text{Bzo-t-Bu}$ (HBzo-t-Bu = 4-tert-Butylbenzoic acid; $\text{Cr}_3\text{O-Bzo-t-Bu}$, for short) and $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 1,1,1-tris(hydroxymethyl)ethane (H_3thmp) gives rise to a fascinating heterometallic one-dimensional (1D) coordination framework $[\text{Cr}_2\text{Dy}_3(\text{Bzo-t-Bu})_9(\text{thmp})_2] \cdot 4\text{H}_2\text{O}$ (**1**) which features slow relaxation of the magnetization (*vide infra*). To reach a balance between the structural and magnetic controls, a certain degree of “design” is indeed present in our selection of the starting materials: (i) Cr(III) with moderate spin ground state (*S*) [17] and Dy(III) ions with strong Ising-like magnetic anisotropy [18-19] were selected to favor the creation of an energy barrier for the magnetization reversal in SCMs. (ii) The carboxylate [20] and polyalcohol ligands [21] exhibit abundant versatility and diversity in bridging metal ions and magnetic transmitting, which have been well used to construct single-

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molecule magnets (SMMs) and SCMs. (iii) the Bzo-*t*-Bu ligand with steric effect serves as separator to prevent the extension of coordination framework. With these considerations in mind, we successfully isolated the blue block crystals of **1** and alternating-current (AC) signals indicate the presence of a frequency-dependent slow magnetic relaxation for complex **1**.

2. Experimental

[Cr₂Dy₃(Bzo-*t*-Bu)₉(thmp)₂]₂·4H₂O (**1**) was synthesized by the solvothermal reaction of Cr₃O-Bzo-*t*-Bu, Dy(NO₃)₃·6H₂O and H₃thmp in the presence of triethylamine (TEA) in mixed CH₃CN–H₂O solvent at 140 °C. Detailed experimental method and crystallographic data are summarized in Supporting Information.

3. Results and discussion

3.1 Description of crystal structure

Complex **1** crystallizes in a triclinic system with space group *P*-1 and *Z* = 2. There are two Cr^{III} ions, three Dy^{III} ions, nine Bzo-*t*-Bu[−] ligands and two thmp^{3−} anions in the asymmetric unit of **1**, whose molecular structure is presented in Fig.1. All H₃thmp ligands exhibit the $\mu_4\text{-}\eta^3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2$ -bridging mode and exist in the fully deprotonated form thmp^{3−} (Fig.1a). The coordination mode of Bzo-*t*-Bu[−] groups falls into three categories: the first coordinates to one Dy^{III} and one Cr^{III} ion in *syn-syn*- $\mu_2\text{-}\eta^1\text{:}\eta^1$ -bridging mode (Fig.1b); the second connects two Dy^{III} ions in $\mu_2\text{-}\eta^1\text{:}\eta^2$ -bridging mode (Fig.1c); the third links three Dy^{III} ions in $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -bridging mode (Fig.1d). All Cr or Dy sites are oxygen-coordinated. The octahedral geometry of the Cr(1)/Cr(2) ion is [CrO₆], in which two O_{carboxylate} atoms are from two Bzo-*t*-Bu[−] groups and four O_{hydroxyl} atoms from two thmp^{3−} ligands. Dy(1) ion is coordinated with eight O atoms belonging to five Bzo-*t*-Bu[−] ligands and three O_{hydroxyl} atoms from two thmp^{3−} groups, showing a square antiprism geometry. The Dy(2) center is ten coordinate, and the [O₁₀] coordination atoms are from five $\eta^1\text{:}\eta^1$ -chelating Bzo-*t*-Bu[−] ligands. The Dy(3) ion displays a square antiprism geometry formed by the coordination of five O_{carboxylate} atoms from five Bzo-*t*-Bu[−] ligands and three O_{hydroxyl} atoms from two thmp^{3−} groups. Two thmp^{3−} groups and four Bzo-*t*-Bu[−] ligands bridge two Cr^{III} ions and two Dy^{III} ions to form heterometallic tetrameric [Cr₂Dy₂(thmp)₂(Bzo-*t*-Bu)₄]²⁺ units, which are further bridged by [Dy(Bzo-*t*-Bu)₅]^{2−} units to form multinuclear 1D chain structure (Figure 2). The Cr–O bond distances range from 1.948(7) Å to 2.036 (7) Å, while the Dy–O bond distances are from 2.313(8) Å to 2.588(7) Å. Notably, for the steric hindrance of ligand Bzo-*t*-Bu[−], the introduction of Bzo-*t*-Bu[−] may be favorable to form low-dimensional structure, and the thmp^{3−} ligand with more coordination sites is to the benefit of multinuclear structure.

3.2 PXRD analyses

To confirm the phase purities of complex **1** before magnetic measurements, PXRD analyses was performed. As shown in Fig. S1 in Supporting information, the good consistence between the observed PXRD and the predicted one indicated the phase purities of the sample.

3.3 Magnetic studies

The variable-temperature magnetic susceptibility study of complex **1** was carried out at an applied field of 1000 Oe in the temperature range of 2–300 K, as shown in Fig.3. The observed $\chi_M T$ is 47.6 cm³ K mol^{−1} at 300 K for **1**, which is in agreement with the theoretical value of 46.23 cm³ K mol^{−1} for the unit of three isolated Dy^{III} (42.48 cm³ K mol^{−1}, ⁶H_{15/2}, *g* = 3/4) ions and two non-interacting Cr^{III} ions (3.75 cm³ K mol^{−1}, *s* = 3/2, *g* = 2). Upon cooling, the $\chi_M T$ value of **1** stays essentially constant until 100 K, then followed by an obvious decrease to the minimum value of 26.96 cm³ K mol^{−1} at 2 K, which is mainly ascribed to the overall antiferromagnetic interactions and/or the thermal depopulation of the excited Stark sublevels. The Stark sublevels of Dy^{III} of the anisotropic Dy^{III} ions may be progressively thermally depopulated, leading to a decrease of the $\chi_M T$ value [22]. The temperature dependence of the reciprocal susceptibility (1/ χ_M) obeys the Curie-Weiss law at 2–300 K with *C* = 47.9 cm³ K mol^{−1} and θ = −2.3 K. The negative θ value can not indicate antiferromagnetic interactions, because the crystalfield effect of Dy^{III} or the spin-orbit coupling of heavy rare earth ions are also result in the negative θ value.

The *M* vs. *H* data measured in different magnetic fields at 2 K show a steady increase at low field (< 1 T), and then *M* reaches a value of 21.1 *Nβ* at 2 K and 7 T, far from the theoretical saturated value of 36 *Nβ* for three Dy^{III} (*g* = 4/3, *J* = 15/2) and two Cr^{III} (*g* = 2, *S* = 3/2) (Fig.4). In the high-field region, the increase of magnetization is slow and linear, which may be attributed to the anisotropy of the sample. The magnetic unsaturation even at 7 T may be attributed to the magnetic anisotropy and/or low-lying excited states of Dy^{III} ions [23].

To further explore the magnetic dynamics of **1**, the frequency and temperature dependencies of the alternating current (AC) susceptibilities were collected under a zero direct current (DC) field and a 3 Oe AC magnetic field. As shown in Fig. 5, frequency-dependent out-of-phase signals for complex **1** are observed below 4 K, yet all of the in-phase curves (χ') are almost consistent without peaks, suggesting the slow magnetic relaxation behavior [24], which might be an indication of SCM behavior. However, no peak maximum is found in the technically available temperature range. This may result from that quantum tunneling of the magnetization (QTM) is too fast at the operating limits of our magnetometer. Because slow relaxation of the magnetization is experimentally observed only over a short range of temperature and the absence of maxima in the χ'' vs. *T*, Arrhenius equation cannot be fit to evaluate the energy barrier ($\Delta E/kB$) and the preexponential factor (τ_0).

4. Conclusion

In conclusion, with $[\text{Cr}_3\text{O}(\text{Bzo-}i\text{-Bu})_6(\text{H}_2\text{O})_3]\text{Bzo-}i\text{-Bu}$ precursor as Cr^{III} ion sources, a new $[\text{Cr}_2\text{Dy}_3]$ cluster-based heterometallic one-dimensional (1D) complex has been prepared *via* stepwise strategy. Magnetic measurements indicate weak antiferromagnetic interactions and/or the thermal depopulation of the excited Stark sublevels in the complex **1**. And AC measurements indicate that complex **1** exhibits slow magnetic relaxation.

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Graphical Abstract

Stepwise assembly of heterometallic 3d-4f chain exhibiting slow magnetic relaxation

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Slow Magnetic
Relaxation

A new [Cr₂Dy₃] cluster-based heterometallic one-dimensional (1D) complex has been prepared *via* stepwise strategy. AC measurements indicate that complex **1** exhibits slow magnetic relaxation.

Fig. 1 Binding modes of Bzo-*t*-Bu[−]ligand (turquoise, Cr; pink, Dy; red, O; light green, C;).

Fig. 2 1D chain structure of the complex **1**.

Fig. 3 Temperature dependence of the $\chi_M T$ and χ_M^{-1} curve for **1**. The red lines represent the best fit to the Curie-Weiss law.

Fig. 4 M vs. H plot at 2 K for **1**.

Fig. 5 Temperature dependence of the out-of-phase signals of the ac susceptibility for **1** under a zero dc field ($H_{dc} = 3$ Oe).