



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 Dy(NO₃)₃·6H₂O and Cr₃O-Bzo-*t*-Bu 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.

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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 isolated 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 isonicotine 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

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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 $[\text{Cr}_3\text{O}(\text{Bzo}-t\text{-Bu})_6(\text{H}_2\text{O})_3]\text{Bzo}-t\text{-Bu}$ (HBzo- $t\text{-Bu}$ = 4-*tert*-butylbenzoic acid; $\text{Cr}_3\text{O}-\text{Bzo}-t\text{-Bu}$, 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 $[\text{Cr}_2\text{Dy}_3(\text{Bzo}-t\text{-Bu})_9(\text{thmp})_2] \cdot 4\text{H}_2\text{O}$ (**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-molecule magnets (SMMs) and SCMs. (iii) The Bzo- $t\text{-Bu}$ 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

$[\text{Cr}_2\text{Dy}_3(\text{Bzo}-t\text{-Bu})_9(\text{thmp})_2] \cdot 4\text{H}_2\text{O}$ (**1**) was synthesized by the solvothermal reaction of $\text{Cr}_3\text{O}-\text{Bzo}-t\text{-Bu}$, $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and H_3thmp in the presence of triethylamine (TEA) in mixed $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ 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- $t\text{-Bu}^-$ ligands and two thmp^{3-} anions in the asymmetric unit of **1**, whose molecular structure is presented in Fig. 1. All H_3thmp ligands exhibit the $\mu_4-\eta^3:\eta^2:\eta^2$ -bridging mode and exist in the fully deprotonated form thmp^{3-} (Fig. 1a). The coordination mode of Bzo- $t\text{-Bu}^-$ groups falls into three categories: the first coordinates to one Dy^{III} and one Cr^{III} ion in *syn-syn*- $\mu_2-\eta^1:\eta^1$ -bridging mode (Fig. 1b); the second connects two Dy^{III} ions in $\mu_2-\eta^1:\eta^2$ -bridging mode (Fig. 1c); the third links three Dy^{III} ions in $\mu_3-\eta^2:\eta^2$ -bridging mode (Fig. 1d). All Cr or Dy sites are oxygen-coordinated. The octahedral geometry of the Cr(1)/Cr(2) ion is $[\text{CrO}_6]$, in which two $\text{O}_{\text{carboxylate}}$ atoms are from two Bzo- $t\text{-Bu}^-$ groups and four $\text{O}_{\text{hydroxyl}}$ atoms from two thmp^{3-} ligands. Dy(1) ion is coordinated with eight O atoms belonging to five Bzo- $t\text{-Bu}^-$ ligands and three $\text{O}_{\text{hydroxyl}}$ atoms from two thmp^{3-} groups, showing a square antiprism geometry. The Dy(2) center is ten coordinate, and the

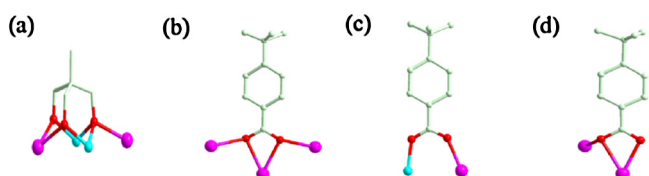


Fig. 1. Binding modes of H_3thmp and Bzo- $t\text{-Bu}$ -ligands (turquoise, Cr; pink, Dy; red, O; light green, C).

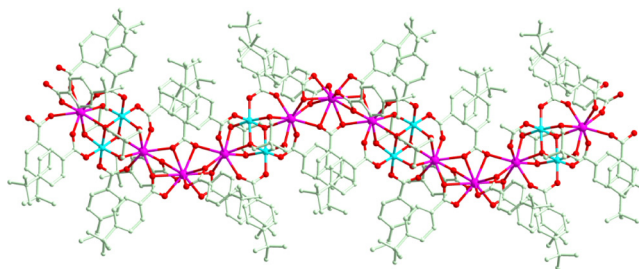


Fig. 2. 1D chain structure of the complex **1**.

$[\text{O}_{10}]$ coordination atoms are from five $\eta^1:\eta^1$ -chelating Bzo- $t\text{-Bu}^-$ ligands. The Dy(3) ion displays a square antiprism geometry formed by the coordination of five $\text{O}_{\text{carboxylate}}$ atoms from five Bzo- $t\text{-Bu}^-$ ligands and three $\text{O}_{\text{hydroxyl}}$ atoms from two thmp^{3-} groups. Two thmp^{3-} groups and four Bzo- $t\text{-Bu}^-$ ligands bridge two Cr^{III} ions and two Dy^{III} ions to form heterometallic tetrameric $[\text{Cr}_2\text{Dy}_2(\text{thmp})_2(\text{Bzo}-t\text{-Bu})_4]^{2+}$ units, which are further bridged by $[\text{Dy}(\text{Bzo}-t\text{-Bu})_5]^{2-}$ units to form multinuclear 1D chain structure (Fig. 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- $t\text{-Bu}^-$, the introduction of Bzo- $t\text{-Bu}^-$ 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 $\text{cm}^3 \text{K mol}^{-1}$ at 300 K for **1**, which is in agreement with the theoretical value of 46.23 $\text{cm}^3 \text{K mol}^{-1}$ for the unit of three isolated Dy^{III} (42.48 $\text{cm}^3 \text{K mol}^{-1}$, $^6\text{H}_{15/2}$, $g = 3/4$) ions and two non-interacting Cr^{III} ions (3.75 $\text{cm}^3 \text{K mol}^{-1}$, $s = 3/2$, $g = 2$). Upon

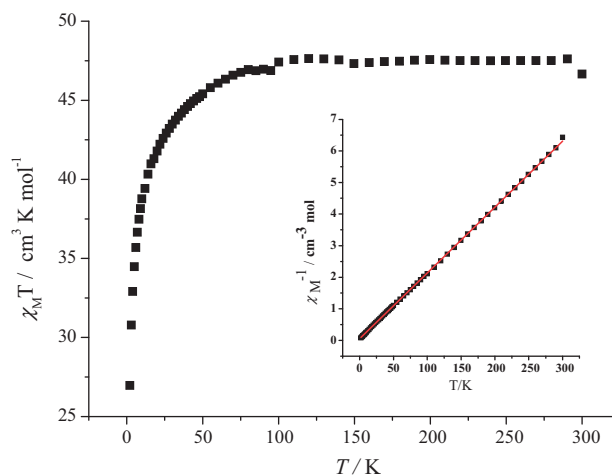


Fig. 3. Temperature dependence of the $\chi_M T$ and χ_M^{-1} curve for **1**. The red lines represent the best fit to the Curie–Weiss law.

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