

Slow magnetization relaxation in a one-dimensional dysprosium-carboxylate compound based on the linear Dy₄ units synthesized ionothermally from a deep-eutectic solvent



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ABSTRACT

A dysprosium-carboxylate coordination polymer, $\{[\text{Dy}_2(2,2'\text{-bpd}^{\text{c}2-})_3(\text{e-urea})(\text{H}_2\text{O})](\text{e-urea})\}_n$ (**1**) (2,2'-bpd^{c2-} = 2,2'-biphenyldicarboxylate and e-urea = ethyleneurea), has been synthesized using a deep-eutectic solvent of choline chloride/e-urea. Four Dy³⁺ ions are linked by the carboxylate oxygen atoms of the 2,2'-bpd^{c2-} ligands to form a linear Dy₄ unit, which is further linked by the carboxylate groups of the 2,2'-bpd^{c2-} ligands to give a rare example of one-dimensional chain based on the linear Dy₄ secondary building units. Detailed static and dynamic magnetic analysis of **1** revealed that **1** exhibits a slow magnetic relaxation behavior.

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Ionothermal synthesis involving the use of ionic liquids (ILs) as reaction media has been employed to prepare crystalline materials recently [1]. ILs have some specific fine-tuning of their solvent properties including polarity, chemical and thermal stability, nonflammability, and negligible vapor pressure, which lead to new types of material that cannot be made in conventional solvents [2]. Deep-eutectic solvent (DES), being one kind of ILs, is a mixture of organic halide salts (e.g., choline chloride) with neutral organic hydrogen bond donors (such as amides, amines, and carboxylic acids) [3]. In addition to their solvent properties similar to the conventional ILs such as imidazolium based ILs, additional advantage of the DESs is their low cost, which is particularly desirable for the large-scale synthesis of new functional materials. Furthermore, the components of the cation, anion, and neutral molecule of the DES can influence the synthetic process through template or direct incorporation into the structures [4]. The DESs acting as solvents and templates have been employed to prepare inorganic frameworks, such as various metal phosphates and phosphonates [5]. However, the use of deep-eutectic mixtures for the preparation of metal-organic framework materials is rarely demonstrated [6]. Present here is a novel Dy-carboxylate coordination polymer synthesized from a DES.

Ionothermal reaction of DyCl₃·6H₂O with 2,2'-biphenyldicarboxylic acid (2,2'-H₂bpd^c) in a mixture of choline chloride with ethyleneurea (e-urea) leads to a novel compound $\{[\text{Dy}_2(2,2'\text{-bpd}^{\text{c}2-})_3(\text{e-urea})(\text{H}_2\text{O})](\text{e-urea})\}_n$ (**1**) (see Supplementary materials) [7]. Compound **1**

is a one-dimensional (1D) chain based on the tetranuclear Dy₄ secondary building units. The experimental PXRD pattern is in good agreement with the simulated one (Fig. S1), indicating the phase purity of the product. The asymmetric unit of **1** contains two Dy³⁺ ions, three 2,2'-bpd^{c2-} ligands, one coordinated water molecule, one coordinated e-urea molecule, and one e-urea solvent molecule. The two crystallographically independent Dy³⁺ ions lie on general positions and display two distinct coordination geometries (Fig. 1). Dy1 is eight-coordinated by eight carboxylate oxygen atoms from five 2,2'-bpd^{c2-} ligands. The coordination polyhedron around Dy1 ion can be attributed to a distorted square antiprism (Fig. 1b). Dy2 is nine-coordinated and surrounded by seven carboxylate oxygen atoms from three chelating carboxylate groups of three 2,2'-bpd^{c2-} ligands and one monodentate carboxylate oxygen of another 2,2'-bpd^{c2-} ligand, one water oxygen atom and one oxygen atom from an e-urea molecule, resulting in a distorted singly capped square antiprism with O4B at the capped position (Fig. 1c). The Dy–O bond distances vary from 2.257(4) to 2.573(4) Å (Table S1), which are comparable to those in other Dy³⁺ compounds [8].

The three crystallographically independent 2,2'-bpd^{c2-} ligands exhibit three different types of coordination modes but all bridges three Dy³⁺ ions (Scheme S1). As shown in Fig. 1, Dy1 and Dy2 ions are bridged by two η²-O atoms (O5 and O11) and one μ₂-carboxylate group to give a dimeric Dy₂ unit with Dy1–O5–Dy2 and Dy1–O11–Dy2 angles of 109.25(13) and 106.96(13)°, respectively. Two symmetry-related Dy₂ units are further linked by a pair of η²-O atoms (O7 and O7A) and a pair of μ₂-carboxylate group to form a centrosymmetric linear Dy₄ unit (Fig. 2), with Dy1–O7–Dy1A angle of 104.13(15)°. The Dy1–Dy2

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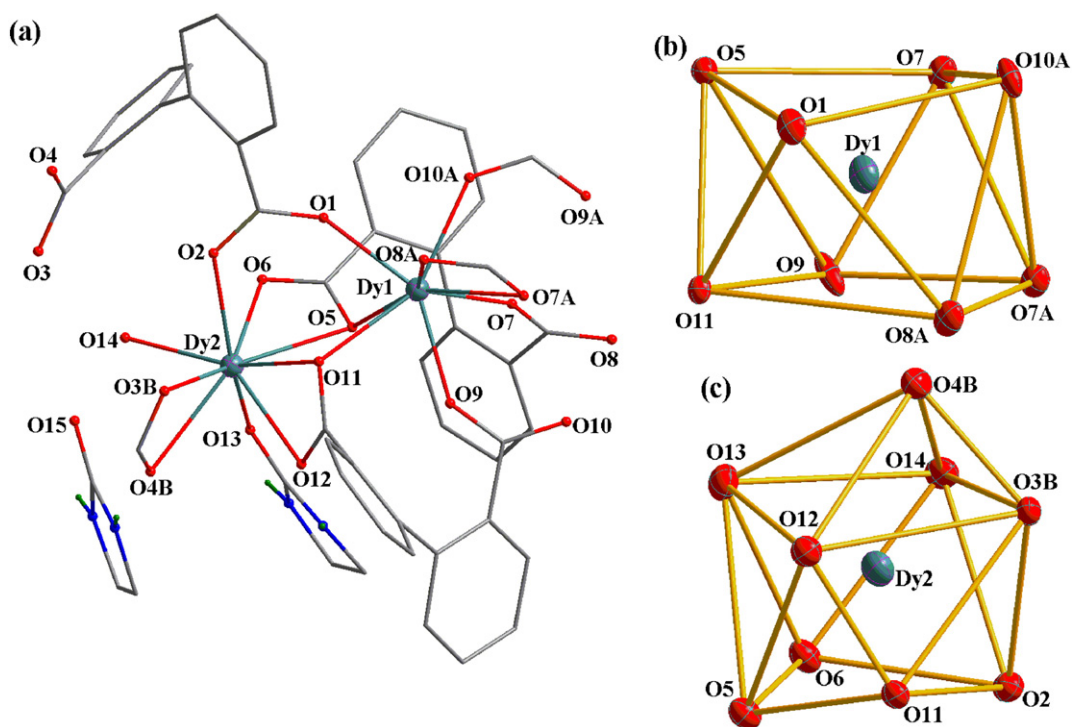


Fig. 1. (a) Coordination environment of Dy centers and (b) and (c) coordination polyhedra around the Dy ions in **1**. Symmetry code: A $-x + 1, -y + 2, -z$; B $-x + 1, -y + 1, -z + 1$.

and Dy1···Dy1A separations are 3.9924(3) and 3.8386(4) Å, respectively, and the Dy2···Dy1···Dy1A angle is 147.927(11)°. The adjacent Dy₄ units are further connected by the 2,2'-bpd²⁻ ligands to form an infinite chain running along (0 -1 1) direction (Fig. 2). The closest Dy···Dy separation between the neighboring Dy₄ units is 5.74 Å within the chain.

Further careful inspection of the packing arrangement reveals that the closest interchain Dy···Dy separation is 11.72 Å, confirming the spatial isolation of the 1D chains (Fig. S2).

Direct current (dc) magnetic susceptibility studies of **1** were performed under a field of 1 kOe over the temperature range of 2–300 K

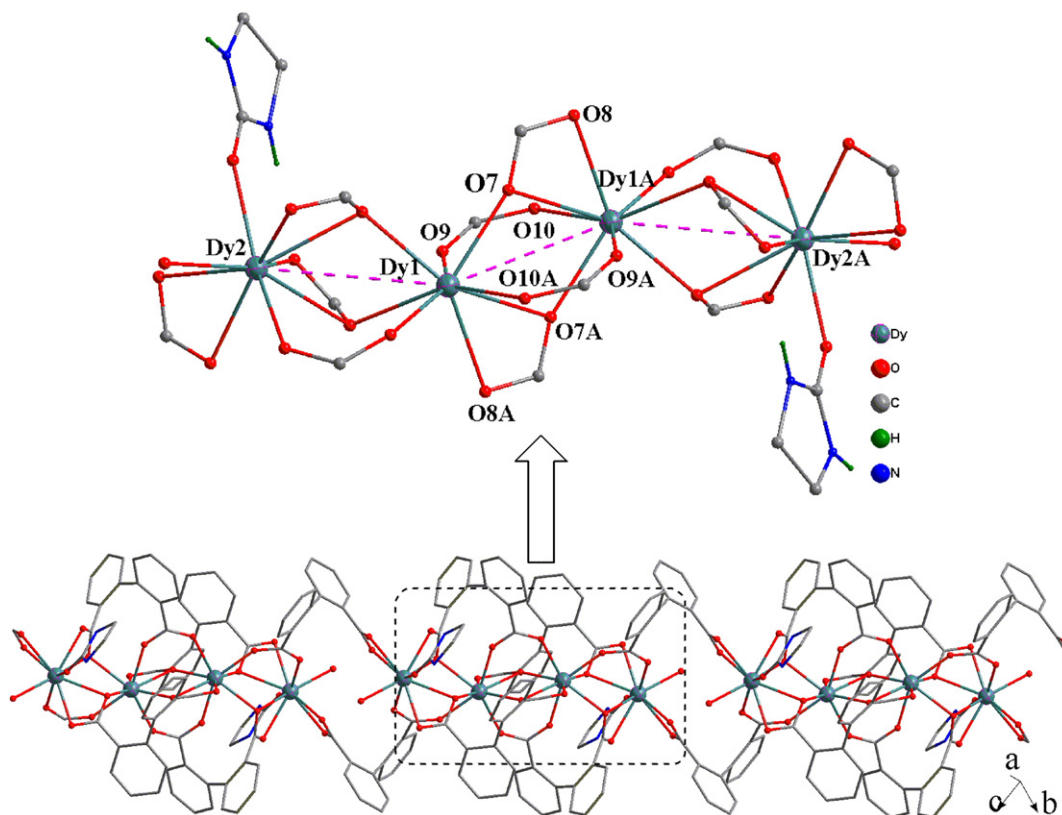


Fig. 2. View of the linear Dy₄ unit (top) and the 1D chain structure of **1** (bottom).

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