

Versatile tetranuclear dysprosium single-molecule magnets



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ABSTRACT

Recent years have witnessed a huge renaissance in the study of the structures and molecular magnetism of 4f-coordination compounds. In particular, lanthanide single-molecule magnets (Ln-SMMs) have become of increasing interest as the anisotropic barrier records have toppled like dominoes. Among them, tetranuclear Dy₄ compounds have played a key role in elucidating the magnetic relaxation dynamics of Ln-SMMs. In this review, the design and magnetic relaxation behavior of tetranuclear Dy₄ SMMs with diverse metal core structural types are discussed in detail with the goal of identifying features relevant to modulating relaxation dynamics of SMMs. The meaningful structure–property relationship obtained will improve our understanding of the magnetic behavior of SMMs and facilitate their potential applications in data storage and processing, essential for the rational design of new molecular-based materials.

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1. Introduction

Single-molecule magnets (SMMs) possessing an energy barrier to the reorientation of their molecular spin opens the intriguing possibility of creating molecular scale devices that store or manipulate information using the orientation of their molecular spin [1–5]. By virtue of high inherent anisotropy as result of unquenched orbital moment, lanthanide complexes present a promising route towards the design of SMMs with high blocking temperatures [6–9]. In particular, dysprosium is viewed as a basic component in the synthesis of such molecules due to the unparalleled single ion anisotropy and the feature of a Kramers ion ($S = 5/2$, $L = 5$, $J = 15/2$) [10,11]. Since the discovery of a triangular Dy₃ complex with toroidal magnetic moments that behaves as a SMM [12–15], research on pure Dy-based polynuclear SMMs with different topologies has flourished with the nuclearity up to 36 [16] and yielded a flurry of groundbreaking results, pushing the frontiers to higher anisotropy barriers and more readily accessed blocking temperature regime [4,17–21].

Notably, tetrametallic Dy-SMMs with different structural types have played important roles in displaying high energy barrier SMM properties and understanding the magnetic relaxation pathway. For example, a centrosymmetric defect cubane is found to show remarkably large anisotropic barrier of 170 K [17]; a linear tetranuclear aggregate with two-step relaxation provides a model

complex to elucidate the relaxation mechanism using a sum of two modified Debye functions [22,23]; furthermore, a preferential relaxation via the second excited state was observed in an oxo-centred octahedral Dy₄K₂ complex [18], which leads to a new record energy barrier. In addition, new Dy₄ complexes with aesthetically pleasing structures are enriching the topological structures. Based on the structural-magnetic relationship, those metallic cores might provide significant insight for structural assembly and magnetic modulations in terms of static and dynamic magnetism. In this respect, systematical study of Dy₄ SMMs with diverse metal core structural types is of fundamental importance both for the search of magnetic systems with superior properties and the understanding of the magneto-structure relationship of Ln-SMMs.

There are several reviews on Ln-SMMs [7–9,24–29], however, an exclusive review on the specific tetrametallic Dy-SMMs is still lack. Here we perform a thorough analysis for tetrametallic dysprosium SMMs with the hopes of shedding some light on magneto-structure relationship and providing references for the search of magnetic systems with superior properties.

2. Survey of Dy₄ SMMs

Interests in Ln-SMMs lead to a steady growth of publications on such compounds every year. Hitherto, more than one hundred examples of polynuclear lanthanide compounds have been reported [8,9], thereinto, 44 compounds are Dy₄ SMMs with different structural types (Table 1). With respect to the metal

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Table 1
The anisotropic barriers of Dy₄ SMMs with diverse metal cores.

Geometry	Dy ₄ -SMMs	U_{eff}/K (H_{dc}/Oe) ^a	Refs.
Linear	[Dy ₄ (L ¹) ₄ (MeOH) ₆] (1)	19.7, 173	[22]
	[Dy ₄ (L) ₄ (HL) ₂ (C ₆ H ₄ NH ₂ COO) ₂ (CH ₃ OH) ₄] (2)	20	[33]
	[Dy ₄ (L) ₂ (C ₆ H ₅ COO) ₁₂ (MeOH) ₄] (3)	17.2	[32]
Zigzag	[Dy ₄ (dhampH ₃) ₄ (NO ₃) ₂] ²⁻ (6)	2.2	[36]
	[Dy ₄ (salen) ₆] (7)	11.9	[37]
	[Dy ₄ (LH) ₂ (LH ₂) ₂ (μ ₂ -η ¹ η ¹ Piv) ₂ (η ¹ Piv) ₄] (8)	43.5(1000), 18.3(1000)	[38]
Rhombus	[Dy ₄ (μ ₃ -OH) ₂ (hmpH) ₂ (hmp) ₂ (N ₃) ₄] (10)	7.0(1)	[44]
	[Dy ₄ (μ ₃ -OH) ₂ (bmh) ₂ (msh) ₄ Cl ₂] (11)	9.7, 170	[17]
	[Dy ₄ (μ ₃ -OH) ₂ (mdeaH) ₂ (piv) ₈] (12)	6.2	[45]
	[Dy ₄ (μ ₃ -OH) ₂ (ampdH ₄) ₂ (piv) ₁₀] (13)	5.4	[46]
	[Dy ₄ (H ₃ L) ₂ (OAc) ₆] (14)	44, 107	[47]
	[Dy ₄ (μ ₃ -OH) ₂ (o-van) ₄ (O ₂ CC(CH ₃) ₃) ₄ (NO ₃) ₂] (15)	5(1)	[48]
	[Dy ₄ (μ ₃ -OH) ₂ L ₂ (acac) ₆] ₃ (16)	22 (1400)	[49]
	[Dy ₄ (μ ₃ -OH) ₂ (μ-OH) ₂ (2,2-bpt) ₄ (NO ₃) ₄ (EtOH) ₂] (18)	55(8)	[51]
	[Dy ₄ (μ-bpt) ₄ (μ ₃ -OH) ₂ (μ-OMe) ₂ (NO ₃) ₄] (19)	80(72)	[52]
	[Dy ₄ (LH) ₂ (μ ₂ -O) ₄] (20)	11.7, 37.7	[53]
	[Dy ₄ L ₂ (μ ₃ -OH) ₂ (μ ₄ -NO ₃)(NO ₃) ₄ (OCH ₃)(H ₂ O)] (22)	28	[55]
	Edge-sharing triangles [2 × 2] grid	[Dy ₄ (HL ³⁻) ₄ (MeOH) ₄] (24)	16 (900)
[Dy ₄ (μ ₄ -OH)(Hhpch) ₈] ³⁻ (25)		30.3, 16; 92 (1000)	[40]
[Dy ₄ (L1) ₄ (μ ₄ -O)(μ ₂ -1,1-N ₃) ₄] (27)		51, 91; 270(1600)	[42]
[(L2-H) ₃ (L2)Dy ₄ (N ₃) ₄ (O)] ³⁻ (29)		110(1) (1800)	[43]
[Dy ₄ (H ₂ L) ₄ (H ₂ O) ₈ ·2DMF] ⁴⁺ (30)		24.9 (2000)	[57]
[Dy ₄ (μ ₃ -OH) ₄ (isonicotinate) ₆ (py)(CH ₃ OH) ₇] ²⁻ (33)		40.2	[63]
Cubane	[Dy ₄ (L) ₄ (μ ₂ -η ¹ η ¹ Piv) ₄] (37)	50.7(1000), 32.8 (1000)	[66]
	[Dy ₄ (OH) ₄ (TBSOC) ₂ (H ₂ O) ₄ (CH ₃ OH) ₄] (38)	15.9	[67]
	[Dy ₄ (μ ₄ -O)(μ-OMe) ₂ (beh) ₂ (esh) ₄] (39)	23.42	[68]
Tetrahedron	[Dy ₄ (μ ₄ -O)L ₂ (C ₆ H ₅ COO) ₆] (40)	ca. 2.3 (1000)	[69]
	[Dy ₄ (3-bpp) ₃ (CO ₃) ₆ (H ₂ O) ₃] (41)	ca. 5.5	[70]
Trigonal pyramid Irregular	[Dy ₄ K ₂ O(O ^t Bu) ₁₂] (42)	692, 316; 842 (after magnetic dilution)	[18]
	[Ln ₄ (μ ₃ -OH)(L ²⁻) ₄ (H ₂ O) ₆] ³⁻ (43)	7.6(1), 83.7(3)	[62]

^a Lattice solvent not listed. U_{eff} values are extracted from measurements in zero dc field, unless followed by a number in parentheses to indicate the strength of the applied field.

centres, the geometries of Dy₄ SMMs can be subdivided into three types: linear and zigzag Dy₄ complexes; planar Dy₄ complexes, such as rhombus/butterfly and [2 × 2] grids; polyhedral Dy₄ complexes, such as cubane, tetrahedron, trigonal pyramid, and other irregular geometries (including oxo-centred octahedron, Y-shaped and ladder). In the following we will review each of these groups of complexes in the order they have been mentioned, without paying attention to the chronological order of their investigation.

2.1. Linear and zigzag Dy₄ complexes

Most linear Dy complexes show strong SMM behavior, which indicates that a linear arrangement of metal centers can rationalize the linkage of the local anisotropies within a molecule [22,30–33]. Especially, the linear Dy₄ SMM from a hydrazone ligand shows the high barrier for magnetization reversal and two-step magnetic relaxation processes [22].

2.1.1. Linear Dy₄ SMMs

In 2010, we reported a Dy₄ compound (Fig. 1)[22] derived from rigid hydrazone ligands showing SMM behavior with a remarkably

large energy barrier. The compound is characterized by a nearly linear Dy₄ core with Dy–Dy–Dy angles of 149.99(1)°, which presents two independent Dy centres, one being in a distorted bicapped trigonal-prismatic geometry and the other in a nearly perfect mono-capped square-antiprismatic environment. The two maxima observed in the out-of-phase ac (alternating current) signals are indicative of the operation of two separate relaxation processes in this compound, with effective energy barriers (U_{eff}) of 19.7 ($\tau_0 = 7.8 \times 10^{-6}$ s) and 173 K ($\tau_0 = 1.2 \times 10^{-7}$ s). Strikingly, the Cole–Cole plots can be nicely fitted by the sum of two modified Debye functions, which is used firstly to explain such a dual relaxation processes. Here the nature of these slower and faster relaxation processes is most likely associated with distinct anisotropic centres.

Two discrete linear Dy₄ compounds **2** and **3** (Fig. 2) have also been prepared by our group [32,33], by using different Schiff-base ligand H₂L¹ and HL², respectively. Obviously, the carboxylate bridges in both compounds show distinct bridging fashions. In compound **2** [33], three different binding modes can be observed for H₂L¹ in its zwitterionic and di-deprotonated forms as η:η:η¹:μ₂-fashion, η¹:η¹:η²:η¹:μ₂-fashion, and η¹:η¹:η¹:

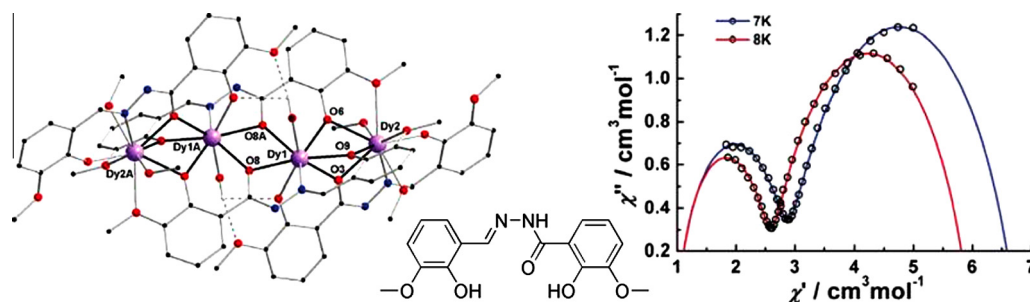


Fig. 1. Molecular structure and the Cole–Cole diagram of complex **1**. Reprinted with the permission from Ref. [22]. Copyright (2010) American Chemical Society.

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