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## Exploring the balance between spin frustration and single-ion effects in triangular Dy<sub>3</sub> complexes†

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We report the synthesis, structures, and magnetic properties of a series of triangular Dy<sub>3</sub> complexes with [Dy<sub>3</sub>(hmc<sub>i</sub>)<sub>3</sub>(MeOH)<sub>6</sub>]·3MeOH·2MeCN·2H<sub>2</sub>O (**1**) and [Dy<sub>3</sub>(hmc<sub>b</sub>)<sub>3</sub>(MeOH)<sub>6</sub>]·3MeOH·1H<sub>2</sub>O (**2**) (H<sub>3</sub>hmc<sub>i</sub> = 2-hydroxy-3-methoxy-5-iodobenzaldehyde hydrazone, H<sub>3</sub>hmc<sub>b</sub> = 2-hydroxy-3-methoxy-5-bromobenzaldehyde hydrazone). These complexes adopt a calixarene-like triangular topology with phenoxide-bridged Dy<sup>3+</sup> ions, leading to near-perpendicular orientation of anisotropic axes relative to the Dy<sub>3</sub> plane. Magnetic studies and theoretical calculations reveal rare examples of Ising spin frustration driven by dipolar interactions, while retaining a zero-field single-molecule-magnet (SMM) behavior. Furthermore, halogen substitutions at the *para* position of the ligands fine-tune the local crystal field environment, enabling modulation of the relaxation dynamics and slow magnetic relaxation profiles. These findings underscore the critical role of ligand design in tailoring spin frustration and optimizing the zero-field SMM performance of triangular Dy<sub>3</sub> complexes.

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## 1. Introduction

Single-molecule magnets (SMMs) are a remarkable class of molecular materials celebrated for their ability to exhibit slow relaxation of magnetization and magnetic hysteresis at the molecular level, driven by strong magnetic anisotropy. Over the years, SMMs have shown tremendous potential for applications in quantum computing, high-density data storage, and spintronic devices.<sup>1–6</sup> While lanthanide-based mononuclear systems have provided fundamental insights into SMM behavior, particularly through precise control of magnetic anisotropy *via* chemical manipulation of crystal-field (CF) splitting, especially for Dy<sup>3+</sup> ions,<sup>7–19</sup> further progress depends on addressing limitations imposed by spin-phonon interactions. In particular, Raman relaxation, which can hinder performance by reducing the blocking temperature, has emerged as a critical bottleneck.<sup>20–23</sup>

In parallel, magnetic interactions between lanthanide ions in polynuclear complexes introduce additional layers of complexity and opportunities for tuning their magnetic properties.<sup>23</sup> These interactions influence key parameters such as blocking temperature and magnetic coercivity, often balancing the subtle dipolar and exchange contributions.<sup>24–30</sup>

Among polynuclear complexes, triangular Dy<sub>3</sub> complexes have emerged as ideal models for exploring the interplay between magnetic anisotropy and intramolecular magnetic interactions.<sup>31</sup> This topology offers an intriguing platform where the spatial arrangement of Dy<sup>3+</sup> ions and their anisotropic axes can create unique magnetic behaviors such as vortex-like arrangements of magnetic moments, resulting in toroidal moments with nonmagnetic ground states but retaining fascinating dynamic properties like slow relaxation and quantum tunnelling.<sup>32–36</sup> Thus, the magnetic interactions between Dy<sup>3+</sup> ions, mediated by the surrounding ligands in combination with the relative orientation of the local anisotropic axis play a critical role in determining the overall magnetic behavior and relaxation dynamics. Beyond their magnetic properties, Dy<sub>3</sub> triangles have also drawn attention for their potential to exhibit magneto-electric coupling, expanding the scope of molecular materials with coupled ferroic properties.<sup>37</sup>

Spin frustration in an Ising triangle, on the other hand, arises from competing antiferromagnetic interactions, which in molecular systems such as triangular trinuclear complexes, lead to nearly degenerate spin ground states.<sup>38–40</sup> The ideal

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frustrated Ising triangle requires a perfectly equilateral geometry, with principal magnetic axes perpendicular to the triangle's plane and sufficiently large  $\text{Dy}^{3+}$ – $\text{Dy}^{3+}$  distances to suppress exchange interactions. In such a configuration, dipolar interactions dominate and induce a frustrated ground state. Yet achieving this necessitates precise control over the orientation of the anisotropic axes as dipolar interactions among highly anisotropic magnetic centers play a critical role in the relaxation dynamics in polynuclear SMMs. Traditionally viewed as either negligible or detrimental, these interactions, when carefully tuned, can effectively govern transition probabilities between low-energy states.<sup>41,42</sup> This highlights their potential as a strategic mechanism for refining relaxation processes and tailoring magnetic properties in complex systems.

In this context, phenoxide-based ligands have been widely utilized for assembling polynuclear SMMs with high energy barriers, offering a robust framework for constructing diverse core topologies.<sup>2,5,16,43–50</sup> Previously, we reported a triangular  $\text{Dy}_3$  complex based on the  $\text{H}_3\text{hnc}$  (1,5-bis(2-hydroxy-3-methoxy-5-nitrobenzylidene)carbonohydrazide) featuring an electron-withdrawing  $\text{NO}_2$  group in the *para* position.<sup>31</sup> This topology features a central  $\text{Dy}_3$  triangle with *para*-substituents projecting outward in a tripod-like configuration below the  $\text{Dy}_3$  plane.

Building on this foundation, the present study extends this design by incorporating halogen substituents. In contrast to our previous work with a  $\text{NO}_2$   $\pi$ -withdrawing group, we utilize halogen substituents, known for their  $\pi$ -donating ability, with the aim to increase the electron density at the phenoxide oxygen and in turn modulate the magnetic anisotropy and relaxation dynamics. By examining the steric and electronic effects introduced by halogen variations, we aim to uncover how these subtle modifications govern the magnetic behavior in two novel triangular  $\text{Dy}_3$  SMMs and in particular their spin frustration. Interestingly, despite differences in ligand substitution and the number of crystallographically distinct  $\text{Dy}^{3+}$  centers, a similar low-temperature regime observed in our earlier study is evident. This finding suggests a consistent underlying behavior in these systems. This work underscores the adaptability of the tripod-like arrangement while offering a strategic framework for optimizing SMM performance through tailored ligand design.

## 2. Experimental

### 2.1. General conditions

All chemicals and solvents were purchased from Alfa Aesar, and used as received without further purification. The 2-hydroxy-5-iodo-3-methoxybenzaldehyde was prepared according to literature procedures by *o*-vanillin reacting with iodine monochloride.<sup>51</sup> The 5-bromo-2-hydroxy-3-methoxy-benzaldehyde was prepared according to literature procedures by reacting with *o*-vanillin, sodium acetate and bromine in glacial acetic acid.<sup>52</sup>  $^1\text{H}$  spectra were recorded on a Varian Mercury-400 (400 MHz for  $^1\text{H}$ ) spectrometer. Infrared spectra were recorded on all samples in the solid-state under ambient conditions on a Nicolet iS5

FT-IR spectrometer with iD5-ATR accessory in the 4000–400  $\text{cm}^{-1}$  region.

### 2.2. Synthesis of the ligands ( $\text{H}_3\text{hmci}$ and $\text{H}_3\text{hmcb}$ )

2-Hydroxy-5-iodo-3-methoxybenzaldehyde/5-bromo-2-hydroxy-3-methoxy-benzaldehyde (20 mmol) was added to EtOH (100 mL), followed by the addition of carbohydrazide (10 mmol). The solution was refluxed at 70  $^\circ\text{C}$  for 3 hours. A white precipitate formed as the product, which was collected by filtration after removing the remaining ethanol. The precipitate was washed with water and dried under vacuum.

**$\text{H}_3\text{hmci}$ :** yield = 80.4%. NMR ( $\text{DMSO}-d_6$ , 400 MHz): 10.95 (s, 2H), 8.37 (s, 2H), 7.70 (s, 2H), 7.2 (dd, 2H), 3.81 (s, 6H). IR (ATR  $\text{cm}^{-1}$ ): 1699 (s), 1612 (w), 1592 (w), 1563 (m), 1530 (s), 1485 (s), 1439 (m), 1413 (m), 1350 (m), 1265 (s), 1245 (s), 1213 (s), 1143 (m), 1078 (m), 1017 (w), 943 (w), 842 (w), 832 (w).

**$\text{H}_3\text{hmcb}$ :** yield: 79.2%. NMR ( $\text{DMSO}-d_6$ , 400 MHz): 10.98 (s, 2H), 8.40 (s, 2H), 7.56 (s, 2H), 7.11 (dd, 2H), 3.83 (s, 6H). IR (ATR  $\text{cm}^{-1}$ ): 1605 (w), 1573 (w), 1473 (s), 1449 (m), 1439 (m), 1422 (s), 1402 (w), 1352 (m), 1318 (w), 1214 (s), 1139 (w), 1101 (w), 1074 (s), 1005 (w), 927 (m), 847 (m), 824 (s), 784 (m), 761 (s), 700 (m).

### 2.3. Synthesis of $[\text{Dy}_3(\text{hmci})_3(\text{MeOH})_6]\cdot 3\text{MeOH}\cdot 2\text{MeCN}\cdot 2\text{H}_2\text{O}$ ( $1\cdot 3\text{MeOH}\cdot 2\text{ACN}\cdot 2\text{H}_2\text{O}$ )

To a solution of  $\text{DyCl}_3\cdot 6\text{H}_2\text{O}$  (0.125 mmol) in MeOH/MeCN (11.5 mL/3.5 mL) was added a solution of  $\text{H}_3\text{hmci}$  (0.125 mmol, 0.0762 g), and tetraethylammonium hydroxide (0.5 mmol, 0.205 mL) in MeOH/MeCN (11.5 mL/3.5 mL). The solution was stirred for 1 min and then filtered. The yellow solution was left to settle for one week, after which transparent yellow crystals of **1** were obtained by filtration, washed with ether, and dried *in vacuo*. Complex **1**: yield = 9.31%. IR (ATR  $\text{cm}^{-1}$ ): 1594 (w), 1560 (m), 1488 (s), 1456 (s), 1439 (s), 1379 (s), 1306 (m), 1231 (s), 1212 (s), 1148 (w), 1113 (m), 1078 (m), 1020 (w), 956 (w), 863 (w), 837 (w), 779 (m), 760 (s), 713 (m), 663 (m). Anal. (%) calcd for  $\text{C}_{57}\text{H}_{75}\text{N}_{12}\text{Dy}_3\text{O}_{27}\text{I}_6(1\cdot 6\text{H}_2\text{O})$ : C, 26.24; H, 2.90; N, 6.44. Found: C, 25.99; H, 2.62; N, 6.69. CCDC number: 2412859.†

### 2.4. Synthesis of $[\text{Dy}_3(\text{hmcb})_3(\text{MeOH})_6]\cdot 3\text{MeOH}\cdot 1\text{H}_2\text{O}$ ( $2\cdot 3\text{MeOH}\cdot 1\text{H}_2\text{O}$ )

To a solution of  $\text{Dy}(\text{OAc})_3\cdot 4\text{H}_2\text{O}$  (0.125 mmol) in MeOH (15 mL) was added a solution of  $\text{H}_3\text{hmcb}$  (0.125 mmol, 0.0645 g), and triethylamine (1 mmol, 0.139 mL) in MeOH (15 mL). The solution was stirred for 1 min and then filtered. The yellow solution was left to settle for one week, after which transparent yellow crystals of **2** were obtained by filtration, washed with ether, and dried *in vacuo*. Complex **2**: Yield = 16.56%. IR (ATR  $\text{cm}^{-1}$ ): 1596 (w), 1561 (m), 1541 (w), 1488 (s), 1456 (s), 1440 (s), 1408 (w), 1377 (s), 1304 (m), 1229 (s), 1209 (s), 1147 (w), 1079 (m), 955 (w), 839 (w), 805 (w), 786 (m), 760 (s), 721 (m), 669 (m). Anal. (%) calcd for  $\text{C}_{57}\text{H}_{79}\text{N}_{12}\text{Dy}_3\text{O}_{29}\text{Br}_6(2\cdot 8\text{H}_2\text{O})$ : C, 28.97; H, 3.37; N, 7.11. Found: C, 28.63; H, 3.03; N, 7.22. CCDC number: 2412858.†



## 2.5. X-ray crystallography

Single crystals of complexes **1–2** suitable for X-ray diffraction measurements were mounted on an Oxford Xcalibur Sapphire-3 CCD Gemini diffractometer employing graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å), and intensity data were collected with  $\omega$  scans. The data collection and reduction were performed with the CrysAlisPro software, and the absorptions were corrected by the SCALE3 ABSPACK multiscan method. The space-group determination was based on a check of the Laue symmetry and systematic absences, and it was confirmed using the structure solution. The structure was solved and refined with the Olex2 1.2-ac21 package. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms.

Powder diffraction patterns were collected on a Bruker AXS D8 Advance X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). XRD data were collected within a  $2\theta$  range of 5 to 40°.

## 2.6. Magnetic measurements

Magnetic susceptibility data were collected with a Quantum Design MPMS3 SQUID magnetometer working in the range 1.8–300 K with the magnetic field up to 7 Tesla. The samples were filtered and prepared immediately prior to the magnetic measurements in order to minimize any potential degradation. The data were corrected from the sample holder and the diamagnetic contributions calculated from the Pascal's constants. The AC magnetic susceptibility measurements were carried out in the presence of a 2.5 Oe oscillating field in zero or applied external DC field.

## 2.7. Theoretical calculations

CASSCF calculations were performed with ORCA 6.0<sup>53,54</sup> software using the crystallographic structures without any structural geometry optimization. For  $[\text{Dy}_3(\text{hnc})_3(\text{DMF})_6]^{31}$  the molecular orientation was redefined to properly account for the  $C_3$  symmetry between the  $\text{Dy}^{3+}$  sites, ensuring that this axis was aligned along the  $z$ -direction and perpendicular to the  $\text{Dy}_3$  plane. This redefinition was achieved by transforming the  $Pa\bar{3}$  (205) space group into the  $R\bar{3}$  (148) space group using the transformation matrix  $a - b, b - c, a + b + ca - b, b - c, a + b + ca - b, b - c, a + b + c$  as provided by the Bilbao Crystallographic Server.<sup>55,56</sup> Tolerance for energy convergence is fixed at  $10^{-7} E_h$ . An active space considering the seven 4f orbitals with 9 electrons CAS (9, 7) for all the sextets (21 roots) for spin-orbit coupling using QDPT was considered. The calculations employed the def2 Ahlrichs basis sets: DKH-DEF2-TZVP for all atoms except Dy, for which the SARC2-DKH-QZVP basis set was used, and Y, for which the SARC-DKH-TZVP basis set was applied. The AUTOAUX feature was used to automatically generate auxiliary basis sets within the RIJCOSX approximation to speed up the calculations. Then, the SINGLE\_ANISO and POLY\_ANISO<sup>57</sup> program implemented in ORCA was used to obtain details about the magnetic relaxation.

# 3. Results and discussions

## 3.1. Synthesis and crystal structures

To achieve the goal of synthesizing polynuclear complexes with unique topologies, we use the *o*-vanillin building-block to design ligands with multiple coordination sites (Scheme 1). In our previous study, Dy-based trinuclear SMMs were successfully synthesized using Schiff base ligands incorporating several coordination pockets.<sup>31</sup> Building on this foundation, the ligands in this study were strategically modified with -I and -Br substituents at the *para* position of *o*-vanillin to investigate how subtle changes in ligand chemistry influence magnetic properties while maintaining similar coordination environments.

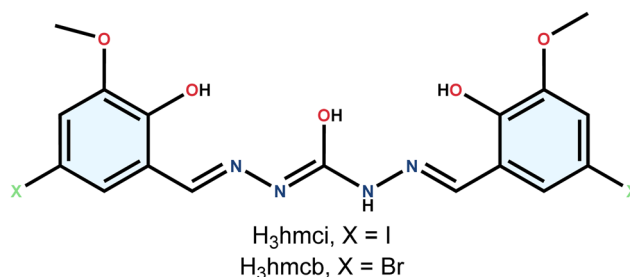
The triangular  $\text{Dy}_3$  complexes,  $[\text{Dy}_3(\text{hmci})_3(\text{MeOH})_6] \cdot 3\text{MeOH} \cdot 2\text{MeCN} \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{Dy}_3(\text{hmcb})_3(\text{MeOH})_6] \cdot 3\text{MeOH} \cdot 1\text{H}_2\text{O}$  (**2**), were synthesized *via* straightforward one-pot reactions conditions.

Both reactions utilized a 1:1 molar ratio of the  $\text{Dy}^{3+}$  precursor and the corresponding Schiff-base ligand ( $\text{H}_3\text{hmci}$  or  $\text{H}_3\text{hmcb}$ ) in methanolic solutions with an excess of base. Methanol served dual roles, acting as the solvent and a terminal ligand occupying coordination sites on the  $\text{Dy}_3$  core.

For complex **1**,  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  was used as the metal precursor, and tetraethylammonium hydroxide (TEAOH, 3.8 equiv.) served as the base to facilitate the deprotonation of  $\text{H}_3\text{hmci}$  and promote the formation of the triangular assembly. While the reaction of  $\text{H}_3\text{hmcb}$  with  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  and TEAOH yielded microcrystalline powders, substituting  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  with  $\text{Dy}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$  and TEAOH with triethylamine ( $\text{NEt}_3$ , 8 equiv.) afforded yellow crystals of **2**.

The choice of ligand substituents (-I in  $\text{H}_3\text{hmci}$  vs. -Br in  $\text{H}_3\text{hmcb}$ ), the base, its quantity, and the  $\text{Dy}^{3+}$  precursor anions (although not incorporated into the structure) all influenced the crystallization behavior. Unfortunately, attempts to crystallize the system with the chlorine-ligand analogue were unsuccessful.

X-ray analysis reveals that complexes **1** and **2** crystallize in the triclinic  $P\bar{1}$  space group with a trinuclear complex in the asymmetric unit (Table S1, ESI†). Both structures consist of triangular  $[\text{Dy}_3(\text{hmci}/\text{hmcb})_3(\text{MeOH})_6]$  complexes, where three crystallographically independent  $\text{Dy}^{3+}$  ions, labelled  $\text{Dy}_1$ ,  $\text{Dy}_2$ , and  $\text{Dy}_3$ , are interconnected by the central part of the ligand *via* three nitrogen atoms and one alkoxide moiety (Fig. 1 and Fig. S1, ESI†). The intramolecular  $\text{Dy}^{3+}$ - $\text{Dy}^{3+}$  distances range from 5.772 to 5.873 Å in **1**, while slightly shorter ranges are



Scheme 1 Scheme of the  $\text{H}_3\text{hmci}$  and  $\text{H}_3\text{hmcb}$  ligands.



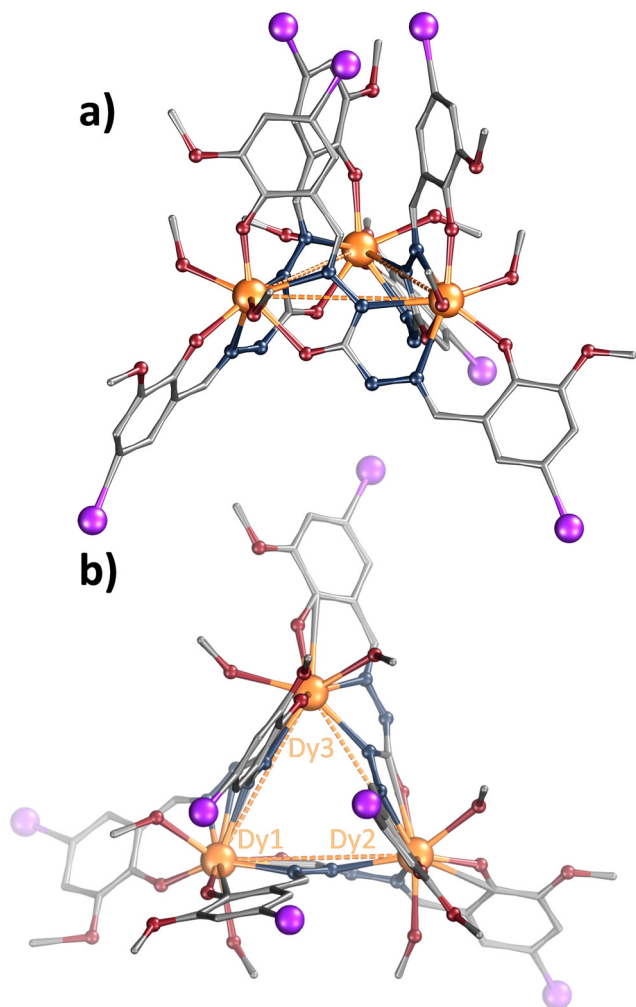


Fig. 1 (a) Molecular structures of **1**. Colour code: orange, Dy; red, O; blue, N; grey, C; purple, I. Hydrogen atoms have been omitted for clarity. (b) View from the top of the  $\text{Dy}_3$  triangle arrangement.

Table 1 Some relevant crystallographic parameters for **1–3**

Compound	Dy–O terminal (Å) out of plane	Dy–O terminal (Å) in-plane	O–Dy–O	Dy–Dy distances (Å)
<b>1</b>	2.184(12)	2.243(12)	116.0(5)	5.772
	2.218(12)	2.240(14)	110.6(5)	5.779
	2.166(12)	2.196(15)	110.8(5)	5.873
<b>2</b>	2.204(5)	2.271(5)	106.32(17)	5.758
	2.226(4)	2.255(5)	114.93(17)	5.798
	2.221(5)	2.213(4)	118.17(18)	5.896

observed in **2** (5.758 to 5.896 Å), indicating subtle structural variations (Table 1). Each  $\text{Dy}^{3+}$  ion exhibits eight-coordinate geometry, coordinated by three nitrogen and three oxygen atoms from the hmci/hmcb ligands, along with two methanol molecules. However, SHAPE analysis<sup>58</sup> highlights distinct differences in coordination geometries between complexes **1** and **2** (Table S2, ESI†). In **1**, all  $\text{Dy}^{3+}$  ions adopt a dodecahedral geometry with varying degrees of distortion, with  $\text{Dy}_2$  exhibiting the lowest degree of distortion. In contrast, complex **2** shows

$\text{Dy}_1$  and  $\text{Dy}_2$  in a dodecahedral geometry, while  $\text{Dy}_3$  adopts a distorted biaugmented trigonal prism.

Two short Dy–O(phenoxide) bonds from distinct ligands are notable in both complexes. The Dy–O bonds nearly perpendicular to the  $\text{Dy}_3$  triangular plane measure 2.166–2.185 Å in **1** and 2.199–2.227 Å in **2**, while those within the plane are slightly longer, ranging from 2.196–2.243 Å in **1** and 2.209–2.275 Å in **2**. The angles between these bonds further emphasize the geometric differences, ranging from 105° to 116° in **1** and 106.25° to 118.31° in **2** (Table 1). Hydrogen bonding interactions are evident within the structures and are observed between the ligands and coordinated methanol molecules. The shortest intermolecular  $\text{Dy}^{3+}$ – $\text{Dy}^{3+}$  distance in the crystal is 7.601 Å, indicating a relatively close packing (Fig. S2, ESI†).

PXRD measurements show that the compounds rapidly lose crystallinity upon exposure to air (Fig. S3, ESI†).

### 3.2. Magnetic properties

The magnetic properties of the triangular complexes were investigated using SQUID magnetometry under both static and dynamic conditions.

At room temperature, the  $\chi T$  ( $\chi$  being the molar magnetic susceptibility and  $T$  the temperature) values for complexes **1** and **2**, were determined to be 42.08  $\text{cm}^3 \text{K mol}^{-1}$  and 42.44  $\text{cm}^3 \text{K mol}^{-1}$ , respectively. These values align well with the theoretical value of 42.51  $\text{cm}^3 \text{K mol}^{-1}$  expected for three isolated  $\text{Dy}^{3+}$  ion ( $^6\text{H}_{15/2}$ ) (Fig. 2).

Upon cooling, the thermal dependence of  $\chi T$  reveals a gradual decrease, reaching 27.04  $\text{cm}^3 \text{K mol}^{-1}$  for **1** and 28.02  $\text{cm}^3 \text{K mol}^{-1}$  for **2** at 1.8 K. This decrease is attributed to the thermal depopulation of the  $\pm m_J$  levels, potentially combined with dominant antiferromagnetic interactions between the  $\text{Dy}^{3+}$  ions. The field-dependent magnetization curves, measured up to 70 kOe at 1.8 K, exhibit unsaturated behavior for both complexes, indicative of significant magnetic anisotropy (Fig. 2, inset). The magnetization ( $M$ ) values at 70 kOe are 15.31 N $\beta$

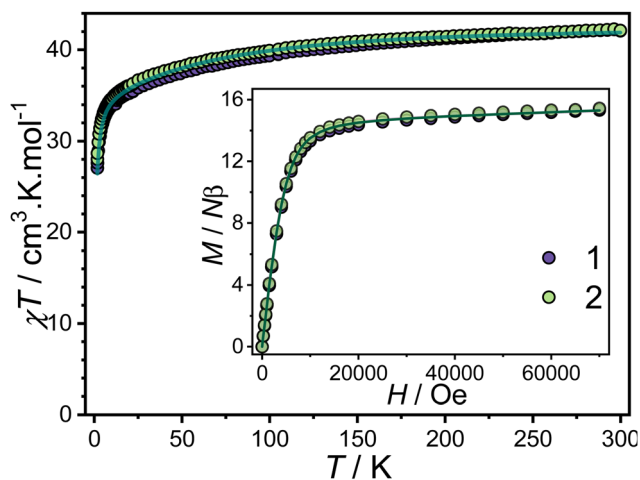


Fig. 2 Temperature dependence of  $\chi T$  under an applied magnetic field of 1000 Oe for **1** and **2**. Inset: Field dependence of the magnetization at 1.8 K. The solid lines represent the fit with POLY\_ANISO.





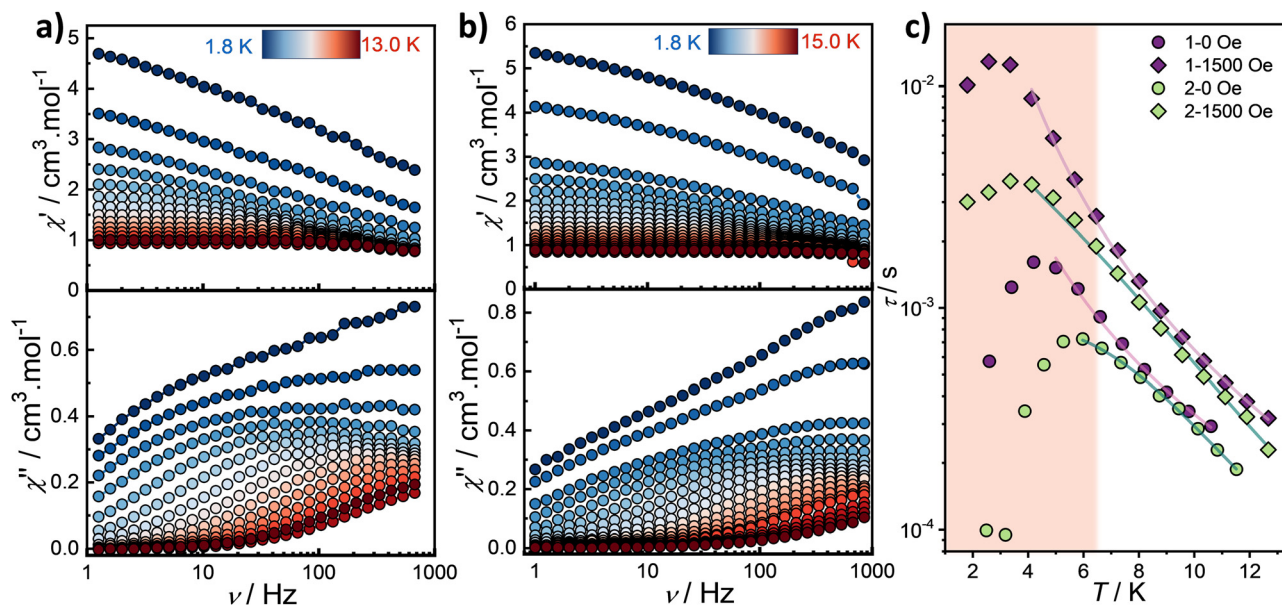


Fig. 3 Frequency dependence of the in-phase ( $\chi'$ ) and out-of phase ( $\chi''$ ) susceptibilities for **1** (a) and **2** (b) under a zero dc-field. (c) Temperature dependence of the relaxation time using the ac susceptibility data. The solid line represents the fit. The low temperature regime is highlighted in coral colour.

for **1** and  $15.44 \text{ N}\beta$  for **2**, consistent with the presence of CF effects.

The magnetic hysteresis loops, measured at 1.8 K, display an opening for both complexes, suggesting the presence of slow relaxation dynamics (Fig. S4, ESI†). Notably, the hysteresis loop for complex **1** is slightly wider compared to that of complex **2**, suggesting distinct relaxation profiles.

The occurrence of slow relaxation of the magnetization was investigated using alternating current (ac) measurements. Under zero dc field, both complexes exhibit a broad out-of-phase ( $\chi''$ ) signal in their ac susceptibility at low temperatures, with no clearly defined maximum (Fig. 3). Upon heating, the signal sharpens, and a single peak gradually emerges up to 13 K.

In the high-temperature regime, the maximum shifts to higher frequencies, as typically expected for systems exhibiting slow relaxation. However, in the low-temperature regime, the opposite behavior is observed, with the maximum shifting to lower frequencies. This unusual trend could arise from the presence of multiple  $\text{Dy}^{3+}$  crystallographic sites, strong intermolecular interactions or possibly a spin frustrated system which may affect the relaxation dynamics.

While these results are primarily attributed to an intrinsic effect of the molecular triangle, it is important to consider the potential role of intermolecular interactions. However, comparison with our previously reported  $[\text{Dy}_3(\text{hnc})_3(\text{DMF})_6]$  triangle which shows even larger intermolecular  $\text{Dy}^{3+}$ – $\text{Dy}^{3+}$  separations and lacks solvate molecules,<sup>31</sup> suggests that these are not the dominant factor.

The observed unusual behavior is further confirmed by the Cole-Cole plots, where the data could not be satisfactorily fitted with a generalized Debye model (Fig. S5, ESI†). In the

high-temperature regime, the  $\alpha$  values remain relatively large until approximately 10 K (about 0.2), indicating a broad distribution of relaxation times (Tables S3 and S4, ESI†). This confirms that the relaxation dynamics are more complex than a simple single relaxation model. The relaxation times,  $\tau$ , were estimated from the ac data. The temperature dependence of  $\tau$  clearly confirms the presence of a distinct low-temperature regime, with a decrease of the relaxation time below approximately 6 and 4 K for **1** and **2**, respectively (Fig. 3c). The “high-temperature” thermal dependence of  $\tau$  can be fitted with a Raman process using

$$\tau^{-1} = CT^n. \quad (1)$$

For complex **2**, a QTM term must be included to obtain a pertinent fit (Fig. 3c). The best fit parameters are provided in Table 2 and highlight also differences in the relaxation dynamics between the two complexes. Note that inclusion a thermally activated behavior leads to unrealistic fitting parameters, suggesting that the dynamics in the high temperature regime is indeed dominated by a Raman relaxation.

As the relaxation dynamics, and in particular the QTM, could be significantly influenced by dc fields, the field dependence of the ac susceptibility was investigated at 2 K (Fig. S6, ESI†).

Table 2 Fit parameters of the temperature dependence of the relaxation time for **1** and **2**

Compound	$n$	$C \text{ (s}^{-1} \text{ K}^{-n}\text{)}$	$\tau_{\text{QTM}} \text{ (s)}$	$A \text{ (s}^{-1} \text{ K)}$
<b>1</b> (0 Oe)	$2.34 \pm 0.05$	$14 \pm 1$	—	—
<b>1</b> (1500 Oe)	$3.06 \pm 0.03$	$1.3 \pm 0.1$	—	—
<b>2</b> (0 Oe)	$4.4 \pm 0.2$	$0.09 \pm 0.04$	$(8.6 \pm 0.4) \times 10^{-4}$	—
<b>2</b> (1500 Oe)	$4.6 \pm 0.4$	$0.03 \pm 0.02$	—	$63 \pm 12$

Both complexes exhibit intricate behavior, with an increase in relaxation time up to approximately 1500–2000 Oe, after which a plateau in  $\chi''$  is observed, preventing further analysis of the relaxation time (Fig. S7, ESI†). For direct comparison between the two complexes, a dc field of 1500 Oe was selected to study its effect on the relaxation dynamics. The frequency dependence collected under this dc field reveals a comparable behavior in comparison to the zero-field data but with maximum observed at lower frequency (Fig. S8, ESI†). Subsequent Cole–Cole analysis (Fig. S9 and Tables S5 and S6, ESI†) and extraction of the relaxation time confirm an increase in relaxation time compared to the zero-field data. The temperature dependence of the relaxation time could be modelled in the high temperature regime with a Raman process for complex **1**, while an additional direct process term is needed for complex **2**, using the equation

$$\tau^{-1} = CT^n + AT \quad (2)$$

(Fig. 3c, Table 2). Although the relaxation times for complexes **1** and **2** differ, they exhibit similar temperature-dependent profiles.

The longer relaxation time observed for complex **1** indicates enhanced axiality compared to complex **2**. For a given compound, the relaxation times are comparable under zero-field and dc-field conditions at higher temperatures. At lower temperatures, a clear bifurcation between the zero-field and field-induced relaxation data becomes however apparent.

### 3.3. Theoretical calculations

To further investigate the relaxation dynamics and explain the observed differences between the complexes, *ab initio* calculations were carried out at the CASSCF level using the ORCA package.<sup>53</sup> For each Dy<sub>3</sub> triangles, two Dy<sup>3+</sup> ions in the respective crystallographic sites were replaced by diamagnetic Y<sup>3+</sup>

ions, creating Dy<sub>1</sub>, Dy<sub>2</sub>, and Dy<sub>3</sub> fragments associated with each Dy<sup>3+</sup> center. The results reveal substantial variations in magnetic anisotropy between the different Dy<sup>3+</sup> sites, both within individual triangular complexes and across complexes **1** and **2**.

To provide a clearer understanding, we first analyse the electronic structures of the different Dy<sup>3+</sup> sites in complex **1**, which presents the best magnetic properties. All Dy<sup>3+</sup> sites exhibit substantial axiality, with  $g_z$  values around 19.3 for Dy<sub>1</sub> and Dy<sub>3</sub>, and slightly higher for Dy<sub>2</sub> ( $g_z = 19.57$ ) (Table 3). Wavefunction compositions indicate a dominant contribution (>89%) from the  $m_J = |\pm 15/2\rangle$  state for all the sites (Tables S7–S9, ESI†). However, none of the sites could be considered as perfectly axial ( $g_z \approx 20$ ). Furthermore, despite Dy<sub>2</sub>'s slightly higher axiality, its transverse  $g_x$  and  $g_y$  components were in the same order of magnitude to those of Dy<sub>1</sub> and Dy<sub>3</sub>, as confirmed by the quantitative comparison of QTM rates obtained from SINGLE\_ANISO (Fig. 4). The anisotropic axes of the ground KD for the Dy<sup>3+</sup> sites are nearly perpendicular to the Dy<sub>3</sub> triangular plane (Fig. 5a) but exhibit varying tilt angles (Table S10, ESI†). The angles between the “out-of-plane” phenoxide and “in-plane” phenoxide in association with the Dy-phenoxide bond lengths most likely influence the tilt of the anisotropic axis relative to the Dy<sub>3</sub> triangular plane. The tilting of the anisotropic axes relative to the Dy<sup>3+</sup>–Dy<sup>3+</sup> intranuclear vectors varies across the Dy<sup>3+</sup> sites. Dy<sub>1</sub> shows the most uniform tilting across both Dy<sub>1</sub>–Dy<sub>2</sub> and Dy<sub>1</sub>–Dy<sub>3</sub> directions, with angles remaining close to perpendicular, while Dy<sub>3</sub> exhibits slightly greater variation. Dy<sub>2</sub>, on the other hand, demonstrates the largest angular deviations. These variations in tilt angles emphasize the geometric and electronic diversity among the Dy<sup>3+</sup> sites, which likely influences the dipolar interactions.

Theoretical calculations also reveal differences in the CF splitting across the different centers. Specifically, the first

**Table 3** Energy of the lowest Kramers doublets (KD) and their associated  $g$  tensors on the individual Dy fragments for **1**

KD	Energy (cm <sup>-1</sup> ) Dy <sub>1</sub>	$g$ tensor Dy <sub>1</sub>	Energy (cm <sup>-1</sup> ) Dy <sub>2</sub>	$g$ tensor Dy <sub>2</sub>	Energy (cm <sup>-1</sup> ) Dy <sub>3</sub>	$g$ tensor Dy <sub>3</sub>
1	0	$g_x = 0.0117$ $g_y = 0.0023$ $g_z = 19.3067$	0	$g_x = 0.0083$ $g_y = 0.0134$ $g_z = 19.5708$	0	$g_x = 0.0084$ $g_y = 0.0170$ $g_z = 19.3313$
2	155	$g_x = 0.3623$ $g_y = 0.6687$ $g_z = 15.8018$	179	$g_x = 0.0083$ $g_y = 0.3186$ $g_z = 15.8432$	140	$g_x = 0.3296$ $g_y = 0.6580$ $g_z = 15.3503$
3	247	$g_x = 1.5716$ $g_y = 2.5509$ $g_z = 14.5608$	253	$g_x = 0.7154$ $g_y = 1.6082$ $g_z = 14.3943$	204	$g_x = 0.7776$ $g_y = 1.9322$ $g_z = 14.5719$
4	333	$g_x = 7.9748$ $g_y = 6.8501$ $g_z = 4.4915$	343	$g_x = 3.6996$ $g_y = 5.2254$ $g_z = 9.9122$	299	$g_x = 5.063$ $g_y = 6.1174$ $g_z = 9.1874$
5	412	$g_x = 0.3304$ $g_y = 3.2666$ $g_z = 11.3609$	418	$g_x = 1.4635$ $g_y = 5.4189$ $g_z = 10.8270$	377	$g_x = 0.0843$ $g_y = 4.1231$ $g_z = 11.1017$
6	497	$g_x = 0.0722$ $g_y = 2.3338$ $g_z = 13.3185$	486	$g_x = 0.7708$ $g_y = 3.3058$ $g_z = 14.8958$	461	$g_x = 1.4451$ $g_y = 3.8186$ $g_z = 10.9838$
7	544	$g_x = 1.0455$ $g_y = 1.5273$ $g_z = 16.1839$	528	$g_x = 0.5906$ $g_y = 1.2066$ $g_z = 17.6440$	502	$g_x = 2.0211$ $g_y = 3.7924$ $g_z = 13.5665$
8	589	$g_x = 0.1750$ $g_y = 0.3598$ $g_z = 19.1759$	606	$g_x = 0.0717$ $g_y = 1.2066$ $g_z = 18.5462$	562	$g_x = 0.3038$ $g_y = 0.4998$ $g_z = 19.0740$



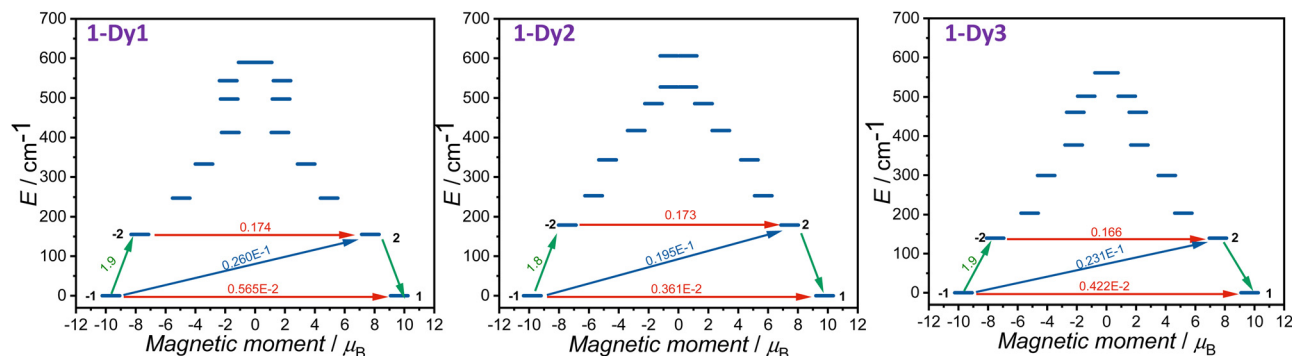


Fig. 4 Energy diagram for low-lying KDs and transition magnetic moment matrix elements<sup>59</sup> (in  $\mu_B$ ) for the connected states (only for the KD1 and KD2) for fragments **1**. For each KD ( $n$ ), the corresponding states ( $-n, n$ ) are placed according to their magnetic moments. The horizontal arrows show the QTM transitions within each doublet, whereas the non-horizontal arrows are spin-phonon transition paths. Only the first KDs are shown here.

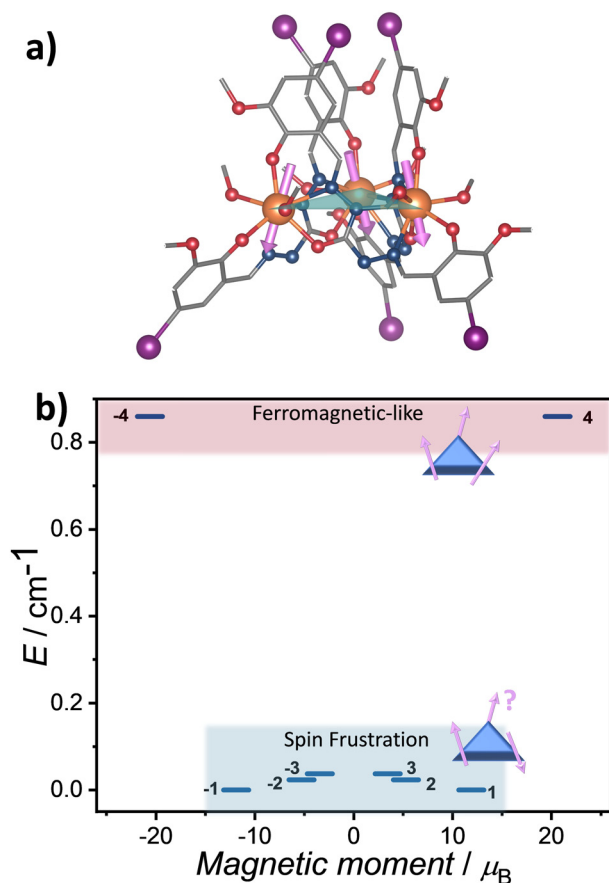


Fig. 5 (a) Orientation of the anisotropic axis (pink) corresponding to the ground KD in **1**. (b) Energy diagram of the coupled states resulting from the dipolar interactions in **1**.

excited KD level ranges from  $140\text{ cm}^{-1}$  ( $\text{Dy}_3$ ) to  $179\text{ cm}^{-1}$  ( $\text{Dy}_2$ ) (Fig. 4 and Table 3). Despite these significant splitting values, a Raman-mediated relaxation is observed, likely due to the limited axiality of both the ground and 1st excited KD for all the  $\text{Dy}^{3+}$  sites.

Although this analysis points out substantial differences between the  $\text{Dy}^{3+}$  sites, the effect of magnetic interaction was

also investigated. Since the local magnetic anisotropy is stronger than the magnetic interactions and nearly perpendicular to the  $\text{Dy}_3$  plane, this system corresponds to a case of Ising spin frustration, characterized by a six-fold degenerate ground state composed of two aligned spins and one inverted spin. To validate this, POLY\_ANISO was employed to obtain details about the magnetic interactions between the  $\text{Dy}^{3+}$  sites. Given the large  $\text{Dy}^{3+}\text{-Dy}^{3+}$  intramolecular distances ( $>5.7\text{ \AA}$ ) and the substantial number of bridging atoms, exchange interactions were neglected, and only dipolar interactions were considered.<sup>34</sup> This allows to nicely reproduce the  $\chi T$  vs.  $T$  and  $M$  vs.  $H$  curves (Fig. 3 and Fig. S10, ESI†). The calculated dipolar interaction matrix (Table S10, ESI†) for **1** suggests a frustrated system. The six-fold degenerate ground state, characterized by two aligned spins and one inverted spin, splits into three closely spaced doublets, located at 0, 0.023, and  $0.037\text{ cm}^{-1}$ , whereas the excited ferromagnetic state is predicted at  $0.859\text{ cm}^{-1}$  (Fig. 5b and Table S12, ESI†). Such small energy differences between the three ground doublets are typically regarded as a hallmark of frustration in triangular systems.<sup>38–40,60</sup>

The computed energy spectrum and corresponding  $g_z$  values provide critical insights into the nature of the coupled states within the  $\text{Dy}_3$  triangle (Fig. 5b). The three low-lying doublets exhibit close  $g_z$  values ranging between 21.52 to 24.45 (Table S12, ESI†). However, their corresponding magnetic moments differ, suggesting varying degrees of spin canting in each state (Fig. 5b). In the ground state, the spins exhibit a moderate degree of canting, resulting in an intermediate magnetic moment of approximately  $11.9\text{ }\mu_B$ .

The second and third doublets also correspond to frustrated configurations, where the canting becomes more pronounced, leading to further reductions in the magnetic moments ( $5.3\text{ }\mu_B$  and  $3.4\text{ }\mu_B$ , respectively). Lastly, the fourth state represents a ferromagnetic-like configuration, yet the spins remain canted rather than perfectly aligned, yielding a reduced magnetic moment of  $20.6\text{ }\mu_B$  instead of the expected  $\sim 30\text{ }\mu_B$  for three Ising-like  $\text{Dy}^{3+}$  ions with ferromagnetic coupling in the absence of canting.

In comparison to **1**, the electronic structures of the  $\text{Dy}^{3+}$  centers in **2** exhibit notable disparities (Tables S13–S16, ESI†).



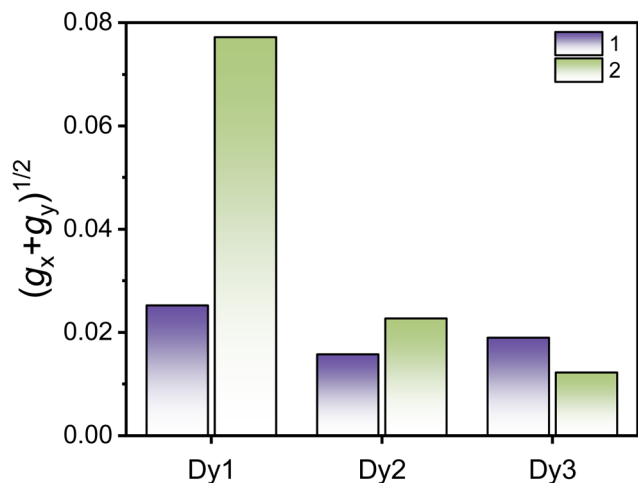


Fig. 6 Bar plot showing the transversal magnetic anisotropy determined by the computed  $\sqrt{g_x^2 + g_y^2}$  for the different  $\text{Dy}^{3+}$  sites in **1** and **2**.

In particular,  $\text{Dy}_1$  exhibits the lowest axiality with a  $g_z$  value of 19.05 whereas  $\text{Dy}_3$  shows the greatest axiality ( $g_z = 19.62$ ). This trend is also reflected in the ground-state wavefunction composition where  $\text{Dy}_1$  shows only 84% of  $m_J = |\pm 15/2\rangle$  state, in contrast to  $\text{Dy}_2$  and  $\text{Dy}_3$  which exhibit 92.6% and 94.4%, respectively (Tables S13–S16, ESI†). Hence, the degree of axiality progressively increases from  $\text{Dy}_1$  to  $\text{Dy}_3$ , as also mirrored by energies of the first KD found at 111, 159 and 177  $\text{cm}^{-1}$  for  $\text{Dy}_1$ ,  $\text{Dy}_2$  and  $\text{Dy}_3$ , respectively. The orientation of the anisotropic axes (Fig. S11, ESI†) and their tilting relative to the  $\text{Dy}_3$  plane are comparable to those observed in **1** (Table S10, ESI†).

However,  $\text{Dy}_1$  exhibits notably higher computed QTM rates (Fig. S12, ESI†), further corroborated by the transverse components of the  $g$ -tensor for the ground doublet. The transverse  $g$ -tensor component, proportional to  $\sqrt{g_x^2 + g_y^2}$ ,<sup>61</sup> highlights the larger transverse anisotropy of  $\text{Dy}_1$  compared to  $\text{Dy}_2$  and  $\text{Dy}_3$ , as well as to the  $\text{Dy}^{3+}$  sites present in complex **1** (Fig. 6).

It turns out that with the exception of the  $\text{Dy}_3$  site, the transverse components are consistently greater in **2**, especially for  $\text{Dy}_1$ . The enhanced transverse components in **2** likely contribute to its reduced SMM performance compared to **1**.

The site-dependent influence of the halogen substituent on the  $\text{Dy}^{3+}$  electronic structure complicates the identification of a clear trend across the series, highlighting the subtle interplay of electronic and steric effects. Future studies focusing on systems with a single  $\text{Dy}^{3+}$  site could help isolate the direct impact of the halogen and potentially reveal more general trends. Additionally, investigating unsubstituted or differently substituted analogues would further elucidate these effects. On the other hand, analysis using POLY\_ANISO reveals a comparable exchange spectrum between **1** and **2**, with the presence of spin frustration (Fig. S13 and Table S12, ESI†).

All these findings suggest that the relaxation dynamics is predominantly of single-ion origin. Indeed, the weak degeneracy breaking of the spin-frustrated states should enable the thermal population of these states, even at low temperatures. Additionally, the conversion between the frustrated states could

occur through a single spin flip on one  $\text{Dy}^{3+}$  center.<sup>39</sup> Therefore, the relaxation dynamics shall be most likely predominantly governed by single-ion effects. Furthermore, the fact that none of the  $\text{Dy}^{3+}$  sites are highly axial is also consistent with the observed Raman relaxation processes at high temperatures and further supports the single-ion origin of the magnetic dynamics in these triangular  $\text{Dy}_3$  complexes.

Nevertheless and to our knowledge, previous examples of frustrated Dy-based Ising triangles do not show the low temperature regime in the ac relaxation profile as observed in **1** and **2**. While it is tempting to attribute this behavior to distinct relaxation pathways arising from the different  $\text{Dy}^{3+}$  crystallographic sites or possible intermolecular interactions, the comparison with our previously reported  $\text{Dy}_3$  triangle  $[\text{Dy}_3(\text{hnc})_3(\text{DMF})_6]$  ( $\text{H}_3\text{-hnc}$ : 1,5-bis(2-hydroxy-3-methoxy-5 nitrobenzylidene) carbonohydrazide) suggests a more complex picture. Unlike **1** and **2**, this compound features a unique crystallographic  $\text{Dy}^{3+}$  site related by a  $C_3$  axis, and also exhibits a drop in relaxation time at low temperatures (Fig. S14, ESI†). To gain further insights, we performed CASSCF calculations to elucidate the electronic structure of  $[\text{Dy}_3(\text{hnc})_3(\text{DMF})_6]$ . Despite differences in substituents and coordinated solvents (MeOH vs. DMF), the CF splitting appears comparable to that in **1** and **2**, with a first excited KD located at 117  $\text{cm}^{-1}$ , while the KD ground-state shows  $g_z = 19.51$  (Table S17 and Fig. S15, ESI†). In  $[\text{Dy}_3(\text{hnc})_3(\text{DMF})_6]$ , the alignment of the anisotropic axes is influenced by the unique crystallographic  $\text{Dy}^{3+}$  site, leading to a less pronounced tilt between the relative axes compared to **1** and **2** (Fig. S16, ESI†). When considering only dipolar interactions, the calculated energy spectrum is closely resembling those of **1** and **2**, displaying three degenerated doublets and a ferromagnetic excited state around 0.86  $\text{cm}^{-1}$ . Furthermore, the significantly large intermolecular  $\text{Dy}^{3+}\text{-Dy}^{3+}$  distances in  $[\text{Dy}_3(\text{hnc})_3(\text{DMF})_6]$  (exceeding 15 Å) suggest that intermolecular interactions are unlikely to drive the low-temperature behavior observed across the  $\text{Dy}_3$  triangles.

To summarize, our findings suggest that single-ion anisotropy likely governs the relaxation behavior in our systems. The moderate magnetic axiality of the  $\text{Dy}^{3+}$  centers is consistent with the observed Raman relaxation processes in the high-temperature range; however, distinct behaviors are observed across the series, including the previously reported compound. This underscores the influence of the substituent and symmetry on the relaxation dynamics. While our analysis using POLY\_ANISO indicates the presence of spin frustration driven by dipolar interactions, as evidenced by the closely spaced ground doublets in the energy spectrum, the direct attribution of the unusual relaxation behavior observed at low temperatures to this phenomenon warrants further investigation, as distinct relaxation pathways arising from the different  $\text{Dy}^{3+}$  sites and/or subtle lattice effects might also contribute to this low-temperature regime. These findings emphasize the need for future research to better capture the underlying dynamics and explore potential avenues for enhancing the magnetic axiality to improve the SMM performance of such frustrated triangular  $\text{Dy}_3$  complexes.





## 4. Conclusions

In this study, we have investigated a series of triangular Dy<sub>3</sub> tripod-like complexes that represent rare examples of Ising spin frustration in a Dy<sub>3</sub> triangle. The unique topology, combined with the nearly perpendicular orientation of the principal magnetic axes to the triangle's plane, leads to a frustrated ground state driven by dipolar interactions, with minimal influence from exchange interactions. This work highlights the critical importance of precise geometric and anisotropic control in achieving such frustration, providing a valuable model for understanding magnetic phenomena in triangular systems.

Remarkably, we observe a distinctive slow relaxation regime at low temperatures in both complexes. While spin frustration is present, its influence on the relaxation dynamics should be limited, with the single-ion effects dominating the high-temperature behavior, highlighting the delicate balance between these two mechanisms. However, comparison with a similar Dy<sub>3</sub> triangle featuring a unique Dy<sup>3+</sup> ion, suggests a more intricate relaxation mechanism at low temperature. Additionally, we demonstrate that halogen substitution at the *para* position of the ligands influences the relaxation dynamics. The halogen substituents modulate the local crystal field, thereby affecting the magnetic anisotropy of the Dy<sup>3+</sup> centers. However, this modulation exhibits site-specific variations within the Dy<sub>3</sub> triangle, reflecting the complex interplay of steric and electronic factors in the ligand environment.

The presence of spin frustration opens promising avenues for future exploration, particularly in fine-tuning the magnetic properties of triangular SMMs through strategic modifications of the ligand framework (including substituents) and by employing techniques such as solvent exchange or other post-synthetic modifications.

## Data availability

Crystallographic data for **1** and **2** has been deposited at the Cambridge Crystallographic Data Centre as Supplementary Publication No 2412859 and 2412858.†

## Conflicts of interest

There are no conflict of interest to declare.

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