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Solvent orientation in the crystal lattice producing distinct magnetic dynamics in two binuclear Dy(III) polymorphs with a polydentate Schiff base ligand†

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Two Dy(III) polymorphs, [Dy(Clapi)]₂·(CH₂Cl₂)₂ (H₃Clapi = 2-(2'-hydroxy-5'-chlorophenyl)-1,3-bis[3'-aza-4'-(2"-hydroxy-5"-chlorophenyl)prop-4'-en-1'-yl]-1,3-imidazolidine), have been obtained, crystallizing in space groups $P2_1/c$ (1a) and C2/c (1b), respectively. Both 1a and 1b have an identical eight-coordinated Dy(III) configuration with D_{4d} symmetry; their only difference is the lattice orientation of the solvent molecule CH_2Cl_2 . Alternating current (ac) magnetic susceptibility measurements reveal that they exhibit distinct magnetic behaviours. Theoretical calculations indicate that the exchange interactions play a vital role in the magnetic behavior of the polymorphs. This work presents a rational model to explore the magnetostructural relationship in both experimental and theoretical aspects of Dy(III) single-molecule magnets.

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Introduction

Single-molecule magnets (SMMs) are well-known molecular materials with potential applications in quantum computing, high-density information storage, magnetic refrigeration, and biomedical fields.¹ Recent advances have shown the viability of Dy(m)-based complexes in generating large spin reversal barriers as a result of their significant magnetic anisotropy arising from the strong unquenched orbital angular momentum and effective spin–orbit coupling.² Any subtle changes to fine-tune the ligand field, such as in solvents³ and pH values,^{4,5} can drastically influence the magnetic behaviour of Dy(m)-based SMMs.

Polymorphism is commonly known as the ability of a compound (or of an element) to crystallize in more than one distinct crystal structure, which is often related to the molecular geometry, interaction and crystal packing.⁶ This phenomenon offers a unique opportunity to study the structure-property relationships of the same compound in different supramolecular environments that differ greatly in physical or chemical

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properties,⁷ which of course could exert a great influence on the magnetic dynamic behavior.⁸

In this paper, we selected the known imidazolidine ring shown in Scheme 1 to prepare the N_4O_3 Schiff base H_3Clapi $(H_3Clapi = 2-(2'-hydroxy-5'-chlorophenyl)-1,3-bis[3'-aza-4'-(2"$ hydroxy-5"-chlorophenyl)prop-4'-en-1'-yl]-1,3-imidazolidine). Asexpected, when a <math>Dy(m) complex is formed, the Dy(m) metal sites are potentially encapsulated by the multi-chelating ligand (H_3Clapi), imparting a steric shield against coordination interference by extraneous solvent molecules and inhibiting dramatic changes in coordination geometry around metal ions. Fortunately, we obtained two polymorphic Dy(m) complexes, $[Dy(Clapi)]_2 \cdot (CH_2Cl_2)_2$ (1a and 1b). They present almost the same molecular structure but have distinct magnetic dynamic behaviours. The impact of polymorphism on the magnetic dynamics is discussed on the basis of the experimental observations and *ab initio* calculations.

Experimental section

Materials and instruction

All commercial reagents and solvents were purchased from Aldrich, Adamas and TCI. ¹H- and ¹³C-NMR spectra were



Scheme 1 Synthesis of the Schiff base ligand H₃Clapi.

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recorded on a Bruker AV-400 or AV-100 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced relative to the residual solvent peak of the NMR solvent (CDCl₃: δ 7.26 (CHCl₃)). ¹³C chemical shifts are reported in parts per million and are referenced to the carbon resonance of the solvent (CDCl₃: δ 77.16). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constants in hertz (Hz). The FT-IR spectra were recorded in the range of 400-4000 cm⁻¹ using KBr pellets on an EQUINOX55 FT-IR spectrophotometer. Elemental analysis (C, H, and N) was conducted on a Perkin-Elmer 2400 CHN elemental analyzer. The phase purity of the bulk and polycrystalline samples was confirmed by powder X-ray diffraction (PXRD) measurements executed on a Rigaku RU200 diffractometer at 60 kV, 300 mA, and Cu K α radiation (l = 1.5406 Å), with a scan speed of 51 min⁻¹ and a step size of 0.02° in 20. Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/DSC STARe thermal analyzer in the range of 25-600 °C under a nitrogen flow at a heating rate of 5 °C min⁻¹. Magnetic measurements were performed in the temperature range 2.0-300 K with an applied field of 1000 Oe, using a Quantum Design MPMS-XL-7 SQUID magnetometer on polycrystalline samples. The diamagnetic corrections for the complexes were estimated using Pascal's constants. Alternating current (ac) susceptibility experiments were performed using an oscillating ac field of 0 Oe at ac frequencies ranging from 1 to 1000 Hz. The magnetization was measured in the field range 0-70 000 Oe.

Synthesis

Schiff base ligand H₃Clapi. To a stirred solution of 5-chlorosalicylaldehyde (2.35 g, 15 mmol) in methanol (20 mL) at 0 °C, trien (0.73 g, 5 mmol) was added dropwise at 0-5 °C. Then, the mixture was heated at 65 °C for 3 h (Scheme 1). After being cooled to room temperature, the yellow solid was separated by filtration and washed with diethyl ether to afford H₃Clapi (2.2 g, 79%). M.p. 150-152 °C. IR (KBr, cm⁻¹): 3190 (s), 3071 (s), 2281 (s), 1604 (s), 1564 (w), 1470 (w), 1410 (m), 1335 (m), 1281 (w), 1200 (m), 1134 (w), 1093 (w),1053 (w), 987 (m), 933 (w), 700 (s), 646 (m), 533 (w), 487 (m). ¹H NMR (400 MHz, CDCl₃) δ 13.15 (s, 1H), 10.51 (s, 1H), 8.25 (s, 1H), 7.39–7.28 (m, 1H), 7.23 (d, J = 2.4 Hz, 1H), 7.04 (d, J = 2.4 Hz, 1H), 6.95 (d, J = 8.8 Hz, 1H), 6.75 (d, J = 8.7 Hz, 1H), 3.87 (s, 1H), 3.67 (t, J = 6.1 Hz, 2H), 3.56–3.44 (m, 1H), 3.03 (dt, J = 12.6, 6.3 Hz, 1H), 2.84–2.69 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 165.16, 159.79, 156.90, 132.28, 130.66, 130.34, 130.28, 123.42, 123.26, 122.52, 119.55, 118.71, 118.58, 89.03, 58.32, 52.77, 51.17.

 $[Dy(Clapi)]_2 \cdot (CH_2Cl_2)_2$ (1a). A suspension of $DyCl_3 \cdot 6H_2O$ (18.85 mg, 0.05 mmol) and H_3Clapi (17.71 mg, 0.05 mmol) in CH_3OH (4.5 mL) and CH_2Cl_2 (10.5 mL) $[V(CH_3OH):$ $V(CH_2Cl_2)] = 3:7$ was treated. The resulting yellow solution was stirred for 2 h and filtered. Pale-yellow block crystals were gathered after one week in 32% yield (based on Dy(m) salts). Anal. calcd for $C_{54}H_{48}Dy_2N_8O_6\cdot(CH_2Cl_2)_2$ (1612.59): C 41.71, H 3.25, N 6.95; found: C 41.64, H 3.35, N 7.01.

[Dy(Clapi)]₂·(CH₂Cl₂)₂ (1b). A suspension of DyCl₃·6H₂O (18.85 mg, 0.05 mmol) and H₃Clapi (17.71 mg, 0.05 mmol) in CH₃OH (5.0 mL) and CH₂Cl₂ (10.0 mL) [V(CH₃OH): V(CH₂Cl₂)] = 1:2 was treated. The resulting yellow solution was stirred for 2 h and then filtered. Pale-yellow block crystals were gathered after five days in 46% yield (based on Dy(m) salts). Anal calcd for $C_{54}H_{48}Dy_2N_8O_6$ ·(CH₂Cl₂)₂ (1612.59): C 41.71, H 3.25, N 6.95; found: C 41.60, H 3.32, N 6.96.

X-ray crystallography

The crystal data for 1a and 1b have been collected on a Bruker SMART CCD diffractometer using a Mo Ka sealed tube. The program SMART was used for collecting the frames of data, indexing reflections, and determining lattice parameters, SAINT for the integration of the intensity of reflections and scaling, SADABS for absorption correction, and SHELXTL for space group and structure determination and leastsquares refinements on F^2 . The structures were solved by direct methods using the program SHELXS-97 (ref. 9) and refined by full-matrix least-squares methods against F^2 with-SHELXL-97.9 Hydrogen atoms were fixed at calculated positions, and their positions were refined using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The experimental details of crystal data, data collection parameters, and refinement statistics are presented in Table S1,† and the selected bond lengths and angles are summarized in Table S2.†

Results and discussion

Description of the structures

Solvent evaporation of ligand H₃Clapi with DyCl₃·6H₂O in 3 : 7 and 1:2 molar ratios resulted in bulk-like crystals of **1a** and **1b**, respectively (Scheme 2). Single-crystal X-ray diffraction reveals that complex **1a** crystallizes in the monoclinic space group $P2_1/c$, while complex **1b** crystallizes in the monoclinic space group C2/c. For both **1a** and **1b**, the structure consists of a dinuclear Dy(m) unit incorporating two CH₂Cl₂ molecules in the lattice. It is particularly worth mentioning that the orientation of the guest CH₂Cl₂ molecule is different.



Scheme 2 Syntheses of complexes 1a and 1b.

In the guest molecule CH_2Cl_2 , the C coordinates (x, y, z) are (-2.420, 6.518, 10.560) and (-0.268, 5.711, 3.947) (Table S3, ESI†). Also, the distances of Dy–C $(1a-CH_2Cl_2)$ and Dy–C $(1b-CH_2Cl_2)$ are 6.613 and 6.396, respectively. Two phenolate O atoms, from the middle arm of each ligand, act as bridges between two Dy(m) centers, forming the coordination sphere of the sandwich dimer structure. According to continuous-shape measure analysis using the SHAPE 2.0 software (ref. 10) (Table S4, ESI†), the coordination geometry of Dy(m) ions in 1a and 1b can be described as a square antiprism (SAPR-8), but with different distortions from the ideal geometry (Fig. 1). The analysis of the packing arrangement reveals that there are no strong intermolecular forces between neighboring molecules (such as π - π stacking and hydrogen bonds) (Fig. 2–4).

The superposition of the two complexes by laying 1a and 1b at the Dy1 and Dy2 positions shows that the positions of the 14 donor atoms are closely coincident (Fig. 5). The Dy–N (imidazolidine) bond length is approximately 0.3 Å longer than the Dy–N (imine) bond length in both cases (Table S2, ESI†). The Dy–O bond lengths of 1a range from 2.229(4) to 2.330(3) Å, while the minimum and maximum Dy–O bond lengths are 2.223(5) and 2.338(5) Å in complex 1b (Table S2, ESI†). The structures of 1a and 1b disclose distinct packing patterns (Fig. 2–4). The shortest Dy…Dy distance in complexes 1a and 1b is 12.111 Å and 12.575 Å, respectively. Due to the longer Dy–O bond distance (average is 2.320 A) of 1b, the coordination geometry of 1a is closer to a square antiprism.

Magnetic properties

The direct-current (dc) magnetic susceptibilities of **1a** and **1b** have been measured with an applied magnetic field of 1000 Oe between 300 and 2.0 K (Fig. 6). At room temperature, the observed $\chi_{\rm M}T$ values of **1a** and **1b** are 27.89 and 28.02 cm³ K mol⁻¹, respectively, which are in good agreement with the theoretical value of 28.34 cm³ K mol⁻¹ for two non-interacting Dy(m) ions (S = 5/2, L = 5, H = 15/2, g = 4/3).^{11*a*-*d*} As shown in Fig. 6, $\chi_{\rm M}T$ gradually decreases with decreasing



Fig. 1 Coordination environment and local coordination geometry of the Dy(m) ions in **1a** and **1b**. The H atoms are omitted for clarity.



Fig. 2 Packing diagram for complexes 1a and 1b along the a axis.



Fig. 3 Packing diagram for complexes 1a and 1b along the b axis.

temperature in the range of 300–50 K and then further decreases sharply to reach a minimum at 2 K, which could be ascribed to antiferromagnetic coupling between two Dy(m) ions, thermal depopulation of low lying crystal field states and/or magnetic anisotropy.^{11e-i}

The field dependence of the magnetization of complexes 1a and 1b was measured at 2.0 K, 3.0 K and 5.0 K in the field range of 0–70 000 Oe (Fig. S8 and S9†). At 70 000 Oe, the magnetization of 1a and 1b reached maximum values of 10.5 Nβ (1a) and 11.1 Nβ (1b), respectively, which are far from the saturation value (20 Nβ), possibly due to anisotropy and the crystal-field effect at the Dy(m) ion that eliminates the 16-fold degeneracy of the $H_{15/2}$ ground state.¹² Furthermore, *M vs. H/ T* curves at different temperatures do not show coincidence in the high field range, indicating the presence of magnetic anisotropy and/or low-lying excited states.¹³

To further investigate the dynamic magnetic behaviour, alternating current (AC) magnetic susceptibility measurements for complexes **1a** and **1b** were undertaken under zero DC field. No out of-phase (χ''_{M}) peaks were seen in complex **1a** but slight temperature and frequency dependence behaviours were observed (Fig. 7 and S10, ESI[†]). It might be attributed to



Fig. 4 Packing diagram for complexes 1a and 1b along the c axis.



Fig. 5 Superposition of the molecules of **1a** (black) and **1b** (grey). Solvent molecules are omitted for clarity.



Fig. 6 $\chi_M T$ vs. T plots for 1a and 1b. The solid lines correspond to calculated fits to the data.



Fig. 7 Temperature dependence of the in-phase and out-of-phase ac susceptibility signals under 0 Oe dc field for 1a (a and b) and 1b (c and d).

the fast quantum tunneling of magnetization (QTM) normally observed in lanthanide systems.¹⁴ Interestingly, under zerodc field, the ac susceptibilities of 1b showed strong frequency and temperature dependencies, which both reveal the typical features associated with the SMM behaviour. It is noteworthy that the temperature dependence of the out-of-phase ac susceptibility did not reach zero below 4 K, as for most 4f SMMs, which might be indicative of a fast relaxation process that becomes dominant in the lower temperature region.¹⁵ From frequency dependencies of ac susceptibility, we can derive the magnetization relaxation time in the form of $ln(\tau)$ plotted as a function of T^{-1} between 2.0 and 7.0 K (Fig. 8). For 1b, $\ln \tau$ vs. T^{-1} plots are fitted to gain effective energy barriers (U_{eff}) of 24.77 K with a pre-exponential factor (τ_0) of 7.2 × 10⁻⁶. It is worth noting that the strong linear dependence of $\ln \tau$ in the high temperature region is indicative of a dominant Orbach



Fig. 8 (a) Magnetization relaxation time; ln(r) versus T^{-1} plots under zero dc field for **1b**. (b) Cole–Cole diagram at 2 K–7 K under zero dc field for **1b**. The solid lines represent the best fit to the measured results.

relaxation mechanism, whilst in the low temperature region its curvature suggests the presence of other possible relaxation pathways.¹⁶ The temperature independent regime is not observed, indicating that the competing relaxation process cannot be QTM. Therefore, the relaxation occurs *via* the temperature dependent Orbach and Raman mechanisms (Fig. 8). Fitting the data sets with eqn (1) yields $U_{eff(1b)} = 28.58$ K ($\tau_0 = 4.6 \times 10^{-6}$ s). Moreover, the Cole–Cole plots at different temperatures (Fig. 8) give almost perfect semicircles, which is fitted by the generalized Debye model.¹⁷

$$\tau^{-1} = CT^{n} + \tau_{0}^{-1} \exp(-U_{\rm eff}/kT)$$
(1)

Theoretical investigation

To interpret the origins of the divergences, we performed *ab initio* calculations for **1a** and **1b**. Complete-active-space selfconsistent field (CASSCF) calculations on one type of individual Dy(m) fragment for **1a** and **1b** on the basis of X-ray determined geometries have been carried out with the MOLCAS 8.0 (ref. 18) and SINGLE_ANISO¹⁹ programs (see the ESI† for details). The lowest spin–orbit energies and the corresponding *g* tensors of **1a** and **1b** are shown in Table 1. From Table 1, the calculated ground g_z values of the Dy(m) fragments are 18.581 and 18.503, respectively, which are close to 20, showing that the Dy(m)– Dy(m) exchange interactions for **1a** and **1b** can be approximately considered to be of the Ising type.

The close comparison of the *g* components of the ground state between them reveals that the corresponding values (g_x , g_y) for complex **1a** are approximately equal to those of complex **1b** by an order of magnitude, while the g_z value of **1a** (18.581) is slightly larger than that of **1b** (18.503), suggesting that an appreciably higher degree of axiality is present in complex **1a**. Accordingly, the energy separations between the ground and the first-excited doublets for the Dy(m) fragments of **1a** and **1b** are 93.1 and 91.2 cm⁻¹, respectively.

Surprisingly, complex 1b exhibits slow magnetic relaxation, at the same time frequency dependence cannot be observed in complex 1a under 0 Oe, possibly due to exchange interactions between the two Dy ions.

The program POLY_ANISO¹⁹ was used to fit the magnetic susceptibility of **1a** and **1b** using the exchange parameters from Table 2. From Fig. 6, the calculated $\chi_{\rm M}T$ values for them

Table 1 Calculated energy levels (cm⁻¹), $g(g_x, g_y, g_z)$ tensors and m_J values of the lowest Kramers doublets (KDs) of individual Dy(III) fragments for complexes **1a** and **1b**

KDs	1a			1b		
	$E (\mathrm{cm}^{-1})$	g	m_J	$\overline{E\left(\mathrm{cm}^{-1} ight)}$	g	m_J
1	0.0	0.074, 0.191, 18.581	±15/2	0.0	0.073, 0.190, 18.503	±15/2
2	93.1	0.661, 0.938, 14.625	$\pm 13/2$	91.2	0.676, 0.996, 14.430	$\pm 13/2$
3	192.5	2.569, 2.679, 11.229	$\pm 11/2$	185.2	2.239, 2.574, 11.289	$\pm 11/2$
4	292.3	4.926, 5.494, 7.352	$\pm 9/2$	285.9	4.951, 5.604, 7.352	$\pm 9/2$
5	390.1	1.253, 1.675, 11.298	$\pm 3/2$	382.8	1.359, 1.914, 11.218	$\pm 3/2$
6	506.9	0.434, 0.630, 14.790	$\pm 1/2$	500.4	0.543, 0.788, 14.755	$\pm 1/2$
7	664.7	0.006, 0.024, 16.919	$\pm 5/2$	658.5	0.001, 0.027, 16.843	±7/2
8	763.6	0.013, 0.022, 19.253	±7/2	755.2	0.019, 0.033, 19.197	±5/2

are both close to the experimental data.²⁰ From Table 2, the fitted Dy(III)-Dy(III) couplings of the two complexes within the Lines model²¹ are all ferromagnetic, and the total coupling parameters J (dipolar and exchange) were included to fit the magnetic susceptibilities. Herein, the ferromagnetic dipolar interactions, J_{dip} , could be calculated exactly based on the calculated orientations of local anisotropy axes and g tensors, whereas the exchange interactions, J_{exch} , were obtained by fitting the static magnetic data. The J_{dip} of the two complexes display similar values, given that the main magnetic axes on the two Dy(III) ions of 1a and 1b (Fig. S13[†]) are antiparallel to each other due to the antiferromagnetic Dy(m)-Dy(m) interactions and deviate from the Dy-Dy vector by a similar angle (close to 90°). Critically, the pure exchange contribution (J_{exch}) to the interactions is distinct in complex 1a from that in complex 1b. In complex 1b, the exchange interactions are effectively increased to the same order of magnitude and with the same sign to the dipolar interactions, thereby resulting in the total interaction J being larger than that in complex 1a. Moreover, the values (close to 0) of the intermolecular interactions (zJ') of both complexes are almost negligible. Certainly, the enhanced magnetic interactions in complex 1b relative to complex 1a produce a larger energy gap (Table S4[†]) between the two lowest exchange Ising doublets, which greatly increases the difficulty of spin reversal via excited doublets in the low-temperature exchange region. Consequently, the different exchange interactions to the subtle structural variations of 1a and 1b are partly responsible for their different magnetic behaviors.

Discussion of the magnetic variations

It is rare that polymorphic Dy(m) complexes show distinct magnetic behaviours. One phenomenon was observed by

Table 2 Fitted exchange coupling constant J_{exch} , calculated dipole-dipole interaction $J_{dipolar}$ and total J between the Dy(III) ions in **1a** and **1b** (cm⁻¹)

Complex	1a	1b
J _{dipolar}	-2.64	-2.60
Jexch	-0.50	-1.25
J	-3.14	-3.85
zJ'	-0.05	0.03

Zheng et al.,^{8b} in which two polymorphic Dy(m) complexes were reported to exhibit field-induced slow relaxation of magnetization at low temperature with energy barriers of 32.0 K and 83.0 K, respectively. The gap between the energy barriers could originate from the different local environments of the Dy(III) ion. Another example is two Dy(III) polymorphs that show distinct slow magnetic relaxation behaviours, which was reported by You.^{8a} The local ligand-field symmetry of the Dy(m) ion is close to C_{2v} and D_{2d} , and the different magnetic relaxation behaviours may be attributed to the different local environments. In the present work, the Dy(m) centers adopt square antiprism (D_{4d}) geometries in both complexes. The Dy-O and Dy-N distances show little difference in 1a and 1b, whereas the guest CH2Cl2 molecules are arranged in different orientations. The obvious difference between 1a and 1b can be attributed to the slightly different coordination environment as well as the orientation of the uncoordinated CH₂Cl₂ molecules. Magnetic measurements and theoretical calculations indicate that the exchange interactions play a vital role in the magnetic behavior of polymorphs 1a and 1b. Two orientations are mentioned in this article (the C coordinates from the guest molecules CH₂Cl₂: A-type (-2.420, 6.518, 10.560); B-type (-0.268, 5.711, 3.947)), and the magnetic test results indicate that the B-type orientation is good for a better SMM performance because the different orientation (position) of CH₂Cl₂ makes the coordination geometry of the molecule trimmed. As is known to all, small structural changes greatly affect the magnetic behavior of SMMs. From the theoretical calculations, we can see that the two g_z values are approximate; it is shown that the axial anisotropy of the mononuclear Dy in each molecule is close. And by fitting the magnetic susceptibility curve, the obtained J can be seen. J_{ex} has an important influence on the magnetic behavior of such a Dy2 system. Because the intermolecular interaction is close to 0, it can be known that the intermolecular interaction has little effect on this system. Thus, different orientations can fine-tune the molecular structure, thereby altering the intramolecular interactions. According to the theoretical calculations, there is a relatively large difference in the exchange interactions between the two compounds. Thus, different orientations can influence and alter the exchange interactions between the two compounds Dy-Dy, thereby regulating their magnetic behavior.

Conclusions

In summary, both polymorphic Dy(m) complexes have been successfully prepared. The two polymorphs show distinct magnetic behaviors. Temperature and frequency dependencies are slightly observed in complex **1a** under zero-dc field, whereas **1b** shows significant single-molecule magnet behaviour. This work presents the rare example that the magnetic dynamic behaviors of Dy(m) complexes could be fine-tuned by the lattice orientation of solvent molecules, which offers an illuminating insight into the magneto-structural relationship of Dy(m) SMMs.

Conflicts of interest

There are no conflicts to declare.

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