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Bromine-bridged Dy₂ single-molecule magnet: magnetic anisotropy driven by *cis/trans* stereoisomers

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We report the first bromine-bridged dinuclear [Dy(Cy₃PO)₂(μ-Br)(Br)₂]₂·2C₇H₈ single-molecule magnet with an effective energy barrier of 684 K and magnetic hysteresis below 3 K. The asymmetric Dy^{III} centres present two unique stereoisomeric octahedral coordination environments depending on the *cis/trans* disposition of the Cy₃PO ligands, leading to the orthogonality of the easy magnetic axes that annihilate the dipolar interactions.

Recently, research on lanthanide-based single-molecule magnets (SMMs) has made astonishing strides thanks to the increasing knowledge of manipulating the electronic structure of the magnetic centers and some non-traditional ingenious synthetic approaches.¹ Notably, in highly coordinated lanthanide systems, exploiting the symmetry strategy to suppress transverse crystal-field components makes the several complexes entering the club of 1000 K energy barrier.² A substantial leap in molecular magnetic hysteresis above the liquid nitrogen temperature (>77 K) have been recently realized by removing equatorial ligands in an organometallic Dy^{III} metallocenium cation.³ Inspired by the first generation of SMMs, based on 3d transition metals, polynuclear species were also investigated. These systems allow to take advantage of the magnetic interactions to reduce the quantum tunneling of magnetization (QTM).

However, the progress in the development of polynuclear lanthanide-based is relatively slow and the highest relaxation barriers remain in the order of a few hundred Kelvin in some Tb^{III} and Dy^{III} dimers.⁴ These sophisticated architectures are very appealing since they offer the possibility to conserve the highly anisotropic nature of the individual spins while potentially reducing QTM through appropriate magnetic

coupling. The strength of magnetic interactions is highly dependent on the nature of the bridging ligands.⁵ Usually, the Ln–Ln interactions are weak and of a few wavenumbers due to the core-like character of 4f electrons. Remarkably, the diffused electron cloud distribution of soft ligands, such as the S[−] and radical bridges, can effectively infiltrate into the 4f shell of lanthanide ions which are proved excellent in promoting Ln–Ln interactions.^{4c,6} The anisotropy of each monomer controlled by the ligand field remains the key parameter to improve the SMM property since the magnetic relaxation observed for the whole molecule is driven by local single-ion anisotropy.⁷ In polynuclear 4f block species, the weak interactions between metallic centres, of dipolar and/or exchange origin, are only acting as perturbations on single-ion anisotropy.⁸ But manipulating the relative orientations of the local anisotropies to maximize the collective effect for a given size of aggregate is facing severe challenges.⁹ In dimers, one should pay attention not to stabilize a non-magnetic ground state due to the antiferromagnetic arrangement of neighbouring magnetic moments. Such arrangement is governed by fundamental geometrical considerations when dipolar terms dominate.¹⁰ To this end, the design of chemical objects with peculiar structural organization between magnetic moments of lanthanide allows the exploration of the subtle balance between single ion anisotropy and magnetic interactions.

Herein we report an extreme organization with the successful assembly of heavy *p*-block bromine-bridged Dy₂ SMM [Dy(Cy₃PO)₂(μ-Br)(Br)₂]₂·2C₇H₈ (**Dy₂**) (Cy₃PO = tricyclohexylphosphine oxide) with orthogonal magnetic moments. Very intriguingly, the metal ions present two unprecedented stereoisomers within a dimer that differ by the *cis/trans* positions of the two Cy₃PO ligands. The octahedron is completed by the additional four weak Br[−] donors leading to both longitudinally contracted and elongated octahedra. Interestingly, the binuclear asymmetric structure induces dramatically different anisotropies on both Dy^{III} ions. The *cis/trans* disposition of the Cy₃PO ligands and the presence of the Br[−] bridges promote the orthogonal arrangement of the anisotropy axes and therefore almost hide the dipolar interaction in the dimer.

[‡] These authors contributed equally to this work.

Electronic Supplementary Information (ESI) available: Synthetic details, structural data, additional magnetic figures and *ab initio* studies. CCDC 1852215. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

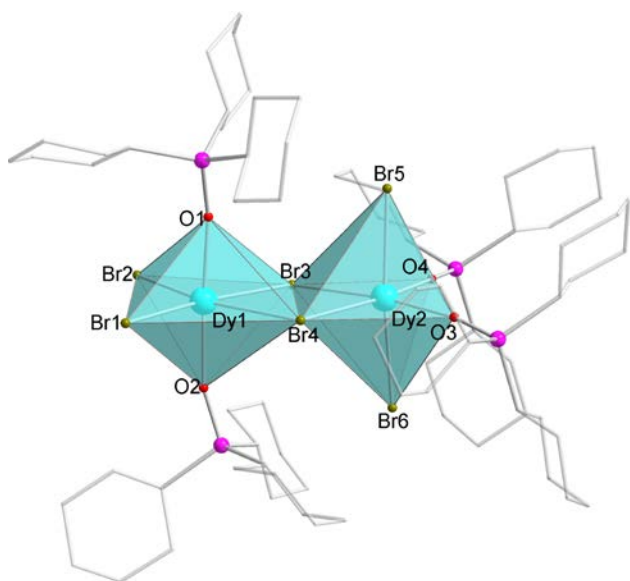


Fig. 1 Structure of Dy_2 (a) and Dy^{III} coordination polyhedra (b). Solvent molecules and hydrogen atoms have been omitted for clarity.

The addition of DyBr_3 and $\text{C}_3\text{H}_7\text{PO}$ at a 1:2 molar ratio in toluene produced white suspension solution in which colorless crystals of Dy_2 were obtained from the filtered extract in 72% yield. Complex Dy_2 crystallizes in the triclinic space group $P\bar{1}$ (Table S1) with the asymmetric unit containing two crystallographically independent Dy^{III} ions, four $\text{C}_3\text{H}_7\text{PO}$ ligands, six Br^- ions and two C_7H_8 solvent molecules. Each Dy^{III} is complexed by four Br^- ions and two $\text{C}_3\text{H}_7\text{PO}$ ligands creating a distorted octahedral environment (Fig. 1; Table S2).¹¹ Dy-O distances are considerably shorter than Dy-Br (Table S3): 2.2 Å vs 2.7~2.9 Å. For Dy1, the two *trans* phosphoryl oxygens of the $\text{C}_3\text{H}_7\text{PO}$ ligands ($\text{O1-Dy1-O2} = 170.84(10)^\circ$) provides an apparent pseudo-linear two coordinated environment to the central Dy1 with strong axial LF. Conversely, for Dy2, the two $\text{C}_3\text{H}_7\text{PO}$ ligands are in *cis* position transversely coordinated to the tetragonal plane. Dy1 make shorter bonds with terminal Br^- than Dy2: $d_{\text{Dy1-Br1}} = d_{\text{Dy1-Br2}} = 2.73$ Å while $d_{\text{Dy2-Br5}} = 2.77$ Å and $d_{\text{Dy2-Br6}} = 2.81$ Å. The distances between bridging bromide and metal centres are comprised between 2.87 and 2.95 Å but still longer for Dy1. 4.46 Å separate Dy1 and Dy2 and Dy-Br-Dy angles are $100.128(12)^\circ$ and $99.684(11)^\circ$. The shortest intermolecular Dy...Dy distance is 11.503(5) Å, indicating well-isolated units for Dy_2 (Fig. S1).

Direct-current (dc) magnetic susceptibility of Dy_2 and isostructural Gd_2 were collected at 1 kOe applied field from 2-300 K (Fig. 2 and S2). The room temperature $\chi_M T$ value of 27.7 and $15.71 \text{ cm}^3 \text{ K mol}^{-1}$ is slightly smaller than the theoretical value of 28.34 and $15.76 \text{ cm}^3 \text{ K mol}^{-1}$ for two uncoupled Dy^{III} ($^6H_{15/2}$, $S = 5/2$, $L = 5$, $g_J = 4/3$) and Gd^{III} ($^8S_{7/2}$, $S = 7/2$, $L = 0$, $g_J = 2$) ions, respectively. Upon cooling, the $\chi_M T$ profile of Dy_2 monotonically decreases to $23.3 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. However, for Gd_2 , the $\chi_M T$ value remains constant with decreasing temperature, with a sharp decrease below 50 K to reach minimum value at 2 K. The isothermal magnetization data of Dy_2 below 5 K reveal a rapid increase at low field and then tends to saturate at 9.7 N β at 50 kOe, in agreement with the

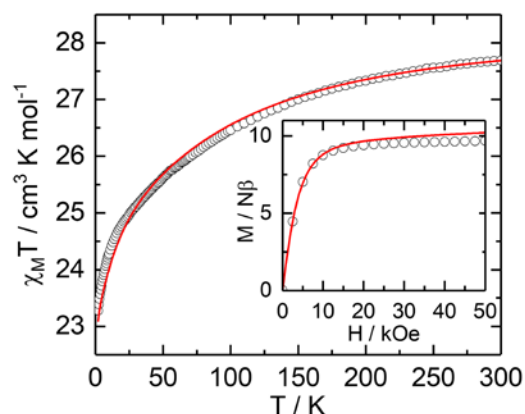


Fig. 2 Thermal evolution of the magnetic susceptibility and evolution of the magnetization with applied magnetic field at 2 K (inset) for Dy_2 . The experimental values are represented as black dots while theoretical data are represented as red lines.

presence of two Dy^{III} ions with $M_J = \pm 15/2$ (10 N β) ground state (Fig. 2, inset and Fig. S3). Simultaneous fitting of the $\chi_M T$ vs T and the M vs H plots with the PHI program¹² leads to $J = -0.029 \text{ cm}^{-1}$ with $g = 2$, thus establishing a weak antiferromagnetic interaction between the Gd^{III} ions (Fig. S2).

The dynamics of the magnetization of Dy_2 was further studied using alternating-current (ac) susceptibility measurements in zero external dc field. A frequency dependent out-of-phase signal (χ_M'') persists up to 40 K (Fig. 3a and S4). A single relaxation time τ is extracted from frequency-dependent ac signals by a generalized Debye model,¹³ giving a narrow relaxation time distribution (α) less than 0.22 (Fig. S5-S6, Table S4). Furthermore, the non-relaxing fraction remains extremely small in the whole temperature range that indicates that the magnetic moments of both sites are involved in the relaxation mechanism and at the same frequency. The application of a magnetic field slows down the

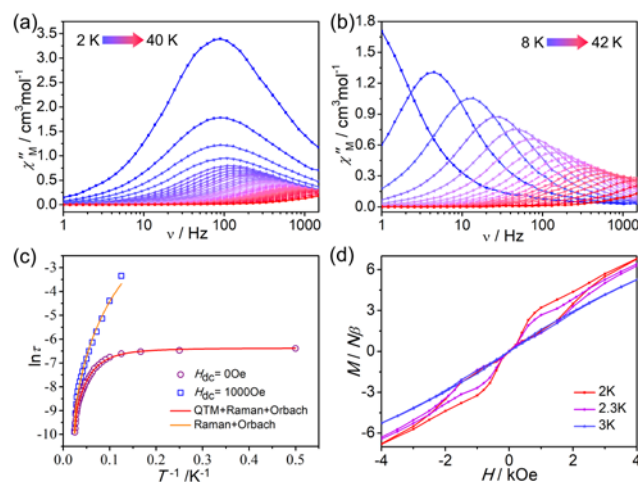


Fig. 3 Frequency-dependent out-of-phase χ_M'' ac susceptibility signals for Dy_2 at (a) zero and (b) 1000 Oe dc field. (c) Temperature dependence of the relaxation time τ in zero and 1000 Oe dc field for Dy_2 . The solid lines represent the best fits of the experimental data to multiple relaxation processes. (d) The M vs H hysteresis profiles of Dy_2 in 2-3 K temperature range, with a magnetic field sweep rate of 8.7 Oe s^{-1} .

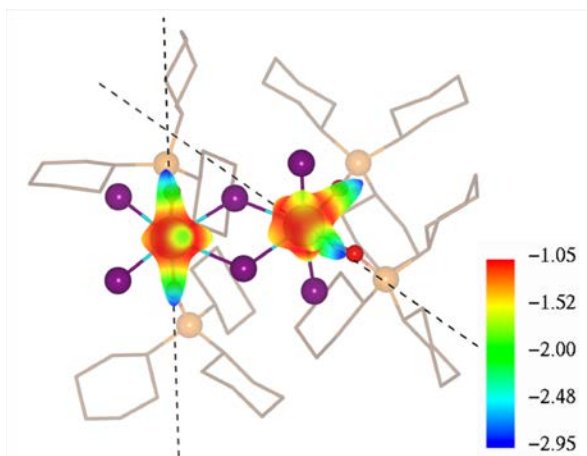


Fig. 4 Representation of the magnetic anisotropy axes and molecular electrostatic potential computed for the ground state KD of each Dy^{III} centre, for Dy_2 .

relaxation processes significantly (Fig. S7). The optimum field at which relaxation is the slowest is estimated at 1000 Oe for which QTM effect is efficiently suppressed. The relaxation is slowed down as shown by a shift in the maxima of χ_M'' to lower frequencies (Fig. 3b and S8-S9). The temperature variation of the relaxation time in zero field can be fitted with contributions from QTM, Raman and Orbach processes with eq. 1 (Fig. 3c) provides the resulting parameters $U_{eff} = 684.1$ K (475.7 cm^{-1}), $\tau_0 = 3.84 \times 10^{-12}$ s, $C = 0.85$ $s^{-1} K^{-2.55}$, $n = 2.55$ and $\tau_{QTM} = 1.69$ ms.

$$\tau^{-1} = \tau_{QTM}^{-1} + CT^n + \tau_0^{-1} \exp\left(-\frac{U_{eff}}{T}\right) \quad (1)$$

Fitting the relaxation time at 1000 Oe with the same eq. 1 without QTM gives a slightly greater U_{eff} of 728.3 K (506.5 cm^{-1}) with $\tau_0 = 2.73 \times 10^{-12}$ s and $C = 0.038$ $s^{-1} K^{-3.34}$, $n = 3.34$ (Fig. 3c, Table S5). The slight differences observed between fitted values may be ascribed to the existence of sizable interactions between the magnetic sites.

As another sign of the slow relaxation, magnetic hysteresis of the magnetization was measured for Dy_2 at a sweep rate of 8.7 Oe s^{-1} (Fig. 3d). Butterfly-shaped hysteresis loops closing at zero field and slightly opening at higher field were observed up to 3 K. This is consistent with the magnetic relaxation times obtained from ac susceptibility data and the presence of quantum tunnelling at zero dc field.

Ab initio SA-CAS(9,7)SCF/RASSI-SO/SINGLE_ANISO calculations are performed for each inequivalent Dy^{III} centre to rationalize the magnetic and electronic properties of Dy_2 (see Supporting Information for details). The calculated eight lowest KDs and local g tensors highlight different behaviours for the two Dy^{III} sites. In the case of Dy_1 (coordinated to the two *trans* Cy_3PO ligands), a pure $M_J = \pm 15/2$ ground state characterized by an Ising-type magnetic anisotropy axis ($g_z = 19.87$ and $g_x = g_y = 0.00$) is observed (Table S6). The anisotropy axis is along the most negatively charged axial Cy_3PO ligands, almost perpendicular (89°) to the tetragonal bromine plane (Fig. 4). This axial repartition of the electronic density around the Dy^{III} ion leads to a large splitting of the ${}^6H_{15/2}$ ground multiplet spanning over 800 cm^{-1} . For Dy_2 , the *cis* disposition of the Cy_3PO ligands lowers the anisotropy character of the g -

tensor ($g_x = 0.06$, $g_y = 0.75$ and $g_z = 18.70$) reflecting a less pure ground state (90% $M_J = \pm 15/2$, Table S7) and a smaller splitting of the ${}^6H_{15/2}$ ground multiplet (around 350 cm^{-1}). The orientation of the magnetic axis still remains along one of the *cis* Cy_3PO moieties, in the tetragonal plane (Fig. 4). These orientations are further supported by the representation of the total molecular electrostatic potential mapped around each Dy^{III} ion using home-made CAMEL program (details in the SI).¹⁴ These results on isolated magnetic centres highlight the influence of the coordination polyhedron on the stabilization of the highly anisotropic $M_J = \pm 15/2$ ground state.

In order to give a more complete description of the magnetic properties, the magnetic interactions occurring in Dy_2 are then considered in the calculations. According to crystallographic data, the intermolecular interactions are neglected due to the large $Dy \cdots Dy$ distances and only intramolecular interactions are taken into account. The magnetic coupling in Dy_2 was estimated by considering dipolar and exchange terms within the Lines model, with an effective spin $1/2$ (eq. 2), as implemented in the POLY_ANISO routine.¹⁵

$$\hat{H}_{ex} = -J^{dip} \hat{S}_1 \hat{S}_2 - J^{ex} \hat{S}_1 \hat{S}_2 \quad (2)$$

First, the intramolecular dipolar interactions are calculated following eq. 3.

$$E = \frac{\mu_0}{4\pi r^3} \left[\mu_1 \cdot \mu_2 - \frac{3}{r^2} (\mu_1 \cdot r)(\mu_2 \cdot r) \right] \quad (3)$$

with μ_1 , μ_2 being the magnetic moment vectors of Dy_1 and Dy_2 respectively, and r being the Dy_1 - Dy_2 vector. The dipolar term therefore depends on both the distance and the orientation of the anisotropy axes. Since the two anisotropy vectors are almost orthogonal (89°), a very low value of the dipolar term is expected. Indeed, the computed dipolar term is -0.13 cm^{-1} leading to the energy splitting observed in Table S8. Then, to complement the qualitative picture of the intramolecular interactions, the effective exchange parameter J^{ex} is fitted

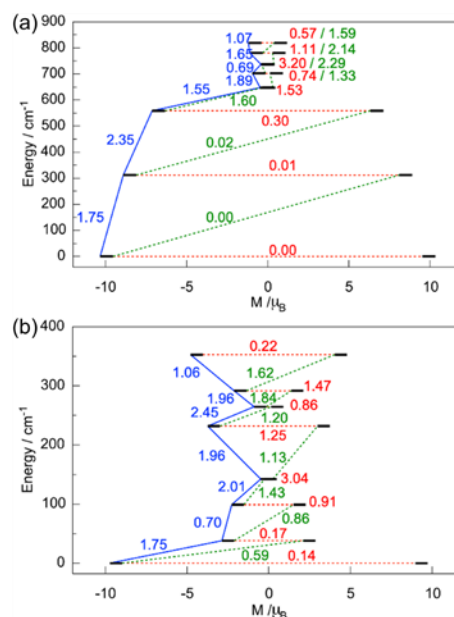


Fig. 5 *Ab initio* computed magnetization blocking barrier for Dy_1 (a) and Dy_2 (b). The dotted green and blue lines show possible Orbach processes, dotted red lines quantum tunnelling processes.

according to the experimental data. The best agreement is found for $J^{ex} = -0.79 \text{ cm}^{-1}$ leading to the exchange spectrum in Table S8. The computed dc magnetic properties are represented in Fig. 2. Superexchange interactions through bromide bridges override dipolar coupling because of the orthogonality between the easy magnetic axes, a spectacular effect of the peculiar *cis/trans* topology in the dimer.

The calculated transition magnetic moment elements, obtained from the *ab initio* single-ion analysis, are depicted in Fig. 5. Let us mention that this interpretation does not directly take into account hyperfine interactions¹⁶ and spin-phonon couplings.¹⁷ For Dy1, the ground and first excited state QTM components are found to be negligible ($0\text{-}10^{-2} \mu_B$) and a significant magnetic axiality is still maintained in the 2nd excited state. Therefore, the most probable relaxation pathway involves the third excited state with an energy barrier of approx. 600 cm^{-1} , slightly higher than the experimental data (about 500 cm^{-1}). On the contrary, a faster relaxation pathway is predicted for Dy2. The calculated transverse transition matrix element between the ground state KD is already large ($0.14 \mu_B$), promoting a faster QTM compared to Dy1. While experimentally we cannot discriminate the two Dy^{III} sites (one single relaxation), the calculations evidence the presence of two drastically different magnetic centres: i) a strongly anisotropic one (Dy1) with the two *trans* Cy₃PO ligands; ii) Dy2, with the LF dictated by the *cis* configuration of the Cy₃PO ligands, inducing a lower magnetic anisotropy character and a faster relaxation mechanism.

In summary, the first bromine-bridged octahedral dinuclear Dy^{III} SMM has been synthesized and characterized. The complex presents a stereoisomeric dimer system with drastically different local anisotropies. Superexchange interactions through bromide bridges override dipolar coupling because of the orthogonality between the easy magnetic axes. Calculations suggest that the observed magnetic relaxation is dominated by the strong axial anisotropy of one dysprosium centre. The second dysprosium ion, with an almost planar anisotropy, is monitored through superexchange interaction. Polymetallic lanthanide systems based on asymmetric building blocks with perpendicular anisotropy arrangements still offer a playground for investigation of relaxation mechanisms in lanthanide SMMs.

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Conflicts of interest

There are no conflicts to declare.

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