Influencing the properties of dysprosium single-molecule magnets with phosphorus donor ligands

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Single-molecule magnets are a type of coordination compound that can retain magnetic information at low temperatures. Single-molecule magnets based on lanthanides have accounted for many important advances, including systems with very large energy barriers to reversal of the magnetization, and a di-terbium complex that displays magnetic hysteresis up to 14 K and shows strong coercivity. Ligand design is crucial for the development of new single-molecule magnets: organometallic chemistry presents possibilities for using unconventional ligands, particularly those with soft donor groups. Here we report dysprosium single-molecule magnets with neutral and anionic phosphorus donor ligands, and show that their properties change dramatically when varying the ligand from phosphine to phosphide to phosphinidene. A phosphide-ligated, trimetallic dysprosium single-molecule magnet relaxes via the second-excited Kramers’ doublet, and, when doped into a diamagnetic matrix at the single-ion level, produces a large energy barrier of 256 cm$^{-1}$ and magnetic hysteresis up to 4.4 K.
The observation of slowly relaxing magnetization in lanthanide bis(phthalocyanine) complexes, LnPC₂, has made tremendous impact in molecular magnetism. Subsequently, hundreds of lanthanide single-molecule magnets (Ln-SMMs) have been reported, with many examples showing very large effective energy barriers to reversal of the magnetization (ΔUeff). Some Ln-SMMs have also been developed for applications in nanoscale devices by, for example, deposition of TbPC₂ onto carbon nanostructures or metallic surfaces. The LnPC₂ SMMs demonstrated that very large Ueff values can occur in monometallic complexes, and this important observation inspired the development of other monometallic Ln-SMMs with ligands such as polyoxometallates and organometallic ligands such as cyclo-octatetraene. Organometallic synthesis offers an alternative strategy for designing Ln-SMMs owing to the diverse range of hard and soft ligands that can be accessed, and such ligands introduce new possibilities for influencing and enhancing the SMM properties.

Phosphorus-ligated Ln-SMMs are unknown; hence we now target the SMM properties of dysprosium and phosphine ligands. Here we show that organo-phosphorus chemistry can be used to influence the dynamic magnetic properties of lanthanide complexes; our observations have general implications for how main group organometallic chemistry can be used to develop new SMMs.

**Results**

**Synthesis and structural studies.** We initially targeted a primary phosphine complex of dysprosium and aimed to sequentially deprotonate the P–H bonds. The adduct [Cp₂Dy−P(H)Mes] (1-Dy) (Cp = η5-C5H5Me, Mes = mesityl) was synthesized by adding mesitylphosphine to tris(methylene)glycolinendienyl dysprosium (Fig. 1). Deprotonation of 1-Dy by 8BuLi gave the trimetallic phosphide-bridged complex [(Cp₂Dy)(µ-P(H)Mes)]3×toluene (2-Dy•toluene). Deprotonation of the P–H bonds in 2-Dy by 8BuLi in toluene produced [Li(thf)]2[(Cp₂Dy)(µ-P-Mes)Li]–thf, which contains the phosphinidene-bridged trimetallic complex [(Cp₂Dy)(µ-P-Mes)Li]2− (3-Dy). The analogous yttrium complexes [Cp₂Y−P(H)Mes] (1-Y), [(Cp₂Y)(µ-P(H)Mes)]3×toluene (2-Y•toluene) and [Li(thf)]2[(Cp₂Y)(µ-P-Mes)Li]–thf, were synthesized in an identical manner. The molecular structures of all compounds were determined by X-ray diffraction; the main features of 1-Dy, 2-Dy and 3-Dy (Fig. 1) are described below, with further details provided in Supplementary Tables 1–3, Supplementary Figs 1–10 and Supplementary Data 1–6.

**Magnetic property measurements.** The static-field (d.c.) magnetic properties of polycrystalline 1-Dy, 2-Dy•toluene and [Li(thf)]2[3-Dy] • thf were measured on a superconducting quantum interference device magnetometer in the temperature range of 1.8–300 K. At 300 K, the value of ZM(T) for 1-Dy, where ZM is the molar magnetic susceptibility, is 12.85 cm³ K mol⁻¹; cooling the sample to 1.8 K produces a gradual decrease in ZM(T), such that a value of 7.93 cm³ K mol⁻¹ is eventually reached (Supplementary Fig. 11). The field (H) dependence of the magnetization (M) for 1-Dy reveals a steep increase up to 1 T, followed by a more gradual increase up to 7 T, where the value of M = 5.09 μB is consistent with a single Dy³⁺ ion with a 6H₁/₂ ground state (Supplementary Fig. 12). The ZMT values for 2-Dy•toluene and [Li(thf)]2[3-Dy] • thf at 300 K are 40.08 and 42.41 cm³ K mol⁻¹, respectively, both of which are close to the predicted values for three uncoupled Dy³⁺ centres, both ZM(T) values decrease gradually down to about 50 K, and then more rapidly to reach 17.81 and 19.47 cm³ K mol⁻¹, respectively, at 1.8 K (Supplementary Fig. 11). For 2-Dy•toluene and [Li(thf)]2[3-Dy] • thf, the magnetization at 1.8 K reaches rapidly up to about 2 T, before following a more gradual increase up to 7 T, where values of M = 16.10 and 16.13 μB are reached. The M(H) data for the two trimetallic complexes are consistent with the expected value for three uncoupled Dy³⁺ ions (Supplementary Fig. 12).

The dynamic (a.c.) magnetic susceptibility properties of the three dysprosium compounds show much greater variation. For 1-Dy, a maximum was observed in the plot of the out-of-phase magnetic susceptibility (χ”) versus a.c. frequency (ν) at 1.8 K, but not at higher temperatures up to the maximum frequency that can be achieved with our susceptometer (Supplementary Fig. 13).
These data indicate rapid relaxation of the magnetization in $^{1}$-Dy above 1.8 K. In contrast, in zero applied d.c. field, the $\chi''(\nu)$ isotherms of $^{2}$-Dy·toluene have well-defined frequency-dependent maxima up to 31 K, which demonstrates SMM behaviour with a large thermal energy barrier (Fig. 2 and Supplementary Figs 14 and 15). The energy barrier for the thermal relaxation in $^{2}$-Dy·toluene was extracted using the relationship $\tau = \tau_0 \exp \left( \frac{U_{\text{eff}}}{k_B T} \right)$, which gave $U_{\text{eff}} = 210(6) \text{ cm}^{-1}$, with a pre-exponential factor of $\tau_0 = 6.53 \times 10^{-9} \text{ s}$. Below about 20 K, the dependence of $\ln \tau$ on $1/T$ weakens and deviates from linearity, but does not become fully temperature independent even at 1.8 K (Fig. 2). This observation implies that other relaxation mechanisms, such as quantum tunnelling of the magnetization and Raman or direct relaxation, occur concurrently with the thermal relaxation process at lower temperatures. In contrast, the $\chi''(\nu)$ isotherms in $[^{3}\text{Li(thf)}_4][^{3}\text{Dy}]$·thf only show maxima below 3.6 K, and the position of the maximum moves only slightly as the temperature is reduced to 1.8 K (Supplementary Figs 16 and 17). The plot of $\ln \tau$ versus $1/T$ for the phosphinidene-bridged complex produces an anisotropy barrier of $U_{\text{eff}} = 13(1) \text{ cm}^{-1}$ ($\tau_0 = 7.75 \times 10^{-7} \text{ s}$), that is, more than an order of magnitude smaller than in phosphide-bridged $^{2}$-Dy·toluene.

To examine the influence of dysprosium–dysprosium interactions, magnetically dilute samples of 5% dysprosium in $^{2}$-Y·toluene and $[^{3}\text{Li(thf)}_4][^{3}\text{Y}]$·thf were prepared; dilution was achieved by mixing $^{1}$-Y and $^{1}$-Dy in a 20:1 ratio and then synthesizing the complexes according to Fig. 1. This enabled isolation of crystalline samples of $^{2}$-Y$_2$Dy·toluene in a matrix of $^{2}$-Y·toluene and, similarly, $[^{3}\text{Li(thf)}_4][^{3}\text{Y}_2\text{Dy}]$·thf in a matrix of $[^{3}\text{Li(thf)}_4][^{3}\text{Y}]$·thf. For both doped trimetallic compounds the a.c. susceptibility data are similar to those measured for the pure samples (Fig. 2, Supplementary Figs 18 and 19), that is, the phosphinidene-bridged complex shows very weak SMM behaviour, while $^{2}$-Y$_2$Dy·toluene is an SMM but with an increased

**Figure 1 | Synthesis and molecular structures.** (a) Synthesis of the yttrium-phosphorus and dysprosium-phosphorus complexes. (b) Thermal ellipsoid representation of the molecular structure of $^{1}$-Dy. (c) Molecular structure of $^{2}$-Dy. (d) Molecular structure of $^{3}$-Dy. Hydrogen atoms are omitted for clarity.
anisotropy barrier of $U_{\text{eff}} = 256(6) \text{ cm}^{-1}$. There is a much clearer and more important difference in the $M(H)$ hysteresis measurements for the undiluted and diluted systems. For 2-Dy·toluene, the $M(H)$ curve at 1.8 K (Supplementary Fig. 20) shows very narrow hysteresis, while hysteresis is found for 2-Y2Dy·toluene up to 4.4 K, with significant widening of the butterfly-shaped loops as the temperature is lowered (Fig. 2). The coercive field for 2-Y2Dy·toluene at 1.8 K is estimated to be $H_c \approx 300 \text{ Oe}$, with a small remanent magnetization of $M_r \approx 0.03 \mu_B$ (sweep rate 2.6 mT s$^{-1}$). The $M(H)$ plot for 2-Y2Dy·toluene also shows steps at $H \approx \pm 1,800 \text{ Oe}$, which is probably due to small amounts of the partially doped di-dysprosium complex 2-YDy. In low magnetic fields, the ground state of 2-YDy2 is defined by antiferromagnetic exchange, but above a certain field strength the ground state changes to ferromagnetic and has a greater magnetic moment, hence the steps in the $M(H)$ curves. The precise field at which the steps are found is consistent with the calculated exchange spectrum from 2-Dy (see below). A feature similar to this has been observed in magnetic dilution studies of di-dysprosium SMMs$^{27,28}$. As $U_{\text{eff}}$ is similar for 2-Dy·toluene and 2-Y2Dy·toluene, the difference in hysteresis must be due to non-thermal relaxation being more important in the undiluted compound.

**Quantum chemical calculations.** Further insight into the electronic structure and the magnetic blocking in the dysprosium complexes was obtained using *ab initio* quantum chemical calculations. Current *ab initio* methods are not suitable for treating several magnetic 4f centres simultaneously; therefore, in the case of 2-Dy and 3-Dy appropriate fragmentation was imposed, hence Lu$^{3+}$ was used in place of neighbouring Dy$^{3+}$ (Supplementary Figs 22–24). All calculations on mono-dysprosium fragments were performed with MOLCAS$^{29}$ and were of CASSCF/RASSI/SINGLE_ANISO type (Supplementary Tables 4–9)$^{30}$. Tables 1 and 2 show the energy spectrum and the magnetic anisotropy of the lowest Kramers’ doublets on individual dysprosium sites of the three compounds.

For the phosphine adduct 1-Dy, the lack of SMM properties is consistent with the absence of strong magnetic axiality of the ground and excited doublets (Table 2). The presence of large $g_{\text{xy}}$ values in the ground state enables fast quantum tunnelling between states with opposite magnetization, destroying any potential blocking of the magnetization$^{31,32}$. This can be rationalized in terms of the molecular and electronic structure of 1-Dy, where the main magnetic axis ($g_x$) lies in a plane defined by three Cp ligands (Supplementary Fig. 26). The electrostatic potential of the ligand field is dominated by the anionic Cp' ligands, which are much closer to dysprosium (average Dy–C$=2.710 \text{ Å}$) than the charge-
neutral phosphine ligand (Dy—P = 3.009 Å). Strong equatorial ligand fields are known to diminish magnetization blocking in Dy³⁺ complexes, hence the weak SMM properties of 1-Dy.

The dysprosium sites in 2-Dy display the strongest magnetic axiality in the ground and excited doublet states, which is combined with the largest splitting of the eight Kramers’ doublets within the ground J = 15/2 manifold of the three systems investigated. The local main magnetic axes (gₐ) in 2-Dy make angles of 69°–72° with the Dy₂ plane (Fig. 3, Table 2). This direction of the magnetization axis on each dysprosium is the result of the strong axial ligand field generated by the two Cp’ ligands, which are closer to dysprosium (average Dy–C = 2.64 Å) than phosphorus (average Dy–P = 2.934 Å), consistent with the electronic properties of closely related metallocene-based SMMs. The very small angles between the anisotropy axes in the ground and first-excited Kramers’ doublets in 2-Dy, combined with their strong magnetic axiality (Table 2 and Fig. 3), are necessary conditions for magnetic relaxation via the second-excited doublet states at higher temperatures.

The calculated energy of the second-excited state (Table 1) gives a reasonable agreement with experiment, being higher than the extracted Uₐeff value by about 20–40 cm⁻¹. Whereas lanthanide SMMs can be designed with ligand environments that promote strongly axial magnetic ground states, targeting SMMs with very large Uₐeff values also requires the excited states to possess main magnetic axes that lie close to co-linear with the ground state, which is challenging. In the case of 2-Dy, the electronic and molecular structures of the individual [Cp’₂Dy(μ-H)(P)Mes] units appear to fit the requirements for a dysprosium SMM in which the ground |m_f| = 15/2 states and |m_f| = 13/2 excited states are indeed co-linear. The strong magnetic axiality of the dysprosium sites is expected to be preserved in the diluted compound Y₃Dy₂, which explains the detection of magnetic hysteresis in this system (Fig. 2).

The dysprosium sites in 3-Dy display a much smaller total splitting of the ground J = 15/2 manifold compared with 2-Dy (Table 1). The different splittings are presumably influenced by subtle differences in the structures of the two complexes, that is, greater distances to the Cp’ ligands (by 0.03–0.09 Å) in 3-Dy, reduced Cₚcent-Dy-Cₚcent angles (by ∼3°) and shorter Dy–P bonds (by 0.10–0.16 Å) together with their greater formal charge. Indeed, the calculated charges on the phosphinidene donor atoms in 3-Dy range from −0.6 to −0.9, compared with the calculated charges of −0.1 to −0.3 on the phosphide donors in 2-Dy.

The closely located phosphinidene ligands and their charge produce a much stronger equatorial ligand field, which counteracts the axial field arising from the Cp’ ligands. Although the ground Kramers’ doublet is still characterized by |m_f| = 15/2, the enhanced equatorial ligand field stabilizes other m_f states and enables greater mixing in 3-Dy relative to 2-Dy. This is reflected in weaker magnetic axiality of the ground state in 3-Dy. Moreover, the first-excited doublets of 3-Dy feature relatively large transverse g-values (gₓ and gᵧ in Table 2), which, combined with the large angles with the ground-state main magnetic axis, leads to fast magnetic relaxation through this doublet at high temperatures.

The ab initio results for the individual metal sites were used to compute the exchange spectrum and the magnetic properties of the trimetallic complexes using the POLY_ANISO program. The fitted Lines exchange parameters are given in Supplementary Table 10. The macroscopic magnetic properties were further computed on the basis of the exchange spectrum. Given the strong magnetic axiality of the ground-state Kramers’ doublets on the dysprosium sites, the magnetic interaction (exchange + dipolar) between them can be described by the non-collinear Ising Hamiltonian in equation 1.

\[
H_{\text{exch}} = -J_{ij}^\text{exch} \hat{s}_i \cdot \hat{s}_j - J_{ij}^\text{dip} \hat{s}_i \cdot \hat{s}_j,
\]

In equation 1, \( J_{ij} = J_{ij}^\text{exch} + J_{ij}^\text{dip} \) is the parameter of the total magnetic interaction between metal sites i and j, including the dipolar and exchange contributions (Supplementary Table 10), \( \hat{s}_i \) and \( \hat{s}_j \) are the local main magnetic axes of the individual dysprosium sites.
is the projection of the pseudo-spin $\frac{1}{2}$, describing the ground Kramers’ doublet on the $i$-th dysprosium site, on the corresponding main magnetic axis $z_i$. The exchange and magnetic dipolar interactions between dysprosium sites in both compounds are antiferromagnetic. For the calculated directions of the main anisotropy axes on the dysprosium sites in 2-Dy and 3-Dy (Fig. 3), the antiferromagnetic exchange and dipolar interactions will stabilize the sixfold degenerate (that is, three Kramers’ doublets), frustrated exchange Kramers’ doublets (Supplementary Table 10). In a frustrated manifold, magnetization blocking of the exchange type is suppressed because all its states can be accessed by reversal of individual magnetic moments on Dy sites (illustrated for 2-Dy in Fig. 4).42 As a consequence, a quantum tunnelling of the magnetization process as fast as those in single-ion complexes is expected. Under these circumstances, the magnetization blocking is expected to arise from individual dysprosium ions. Actually, the magnetic moment reversal on the individual dysprosium ions in the trimetallic compounds 2-Dy and 3-Dy is expected to be faster than in the isostructural complexes containing one single dysprosium, that is, 2-Y$_2$Dy and 3-Y$_2$Dy, because in a frustrated compound the presence of nearest neighbour magnetic sites will enhance the magnetization reversal rate on each magnetic ion.42,43 This is the reason for the clearly enhanced blocking of magnetization and the observation of pronounced hysteresis in in 2-Y$_2$Dy (Fig. 2).42

Magnetization blocking of the exchange type is expected to be efficient only at temperatures not exceeding the exchange splitting, which is the case here because the magnetic coupling constant between two dysprosium ions in 2-Dy is $\sim 4$ cm$^{-1}$ (Supplementary Table 10). The calculated exchange splitting for 2-Dy also provides insight into the steps observed in the $M(H)$ profile for 2-Y$_2$Dy: the exchange splitting in partially doped 2-YDy$_2$ will be about 2 cm$^{-1}$, that is, $\sim 2,000$ Oe, which is in good agreement with the experimentally observed steps at 1,800 Oe.

### Discussion

We have reported a new route to rare-earth complexes of phosphide and phosphinidene ligands. The a.c. susceptibility measurements on phosphide-ligated SMM 2-Dy reveal a large effective energy barrier of $U_{\text{eff}} = 210(5)$ cm$^{-1}$, increasing to 256(6) cm$^{-1}$ on dilution in 2-Y$_2$Dy. In contrast, 1-Dy and phosphinidene-ligated [Li(thf)$_4$]$_2$[3-Dy], and their diluted analogues, do not show prominent SMM properties. Theoretical studies of 2-Dy and 3-Dy identify that the main magnetic axes on the Dy$^{3+}$ ions in the ground Kramers’ doublet have similar orientations approximately perpendicular to the Dy$_3$ plane; even allowing for small differences in the axis orientations (of about 10$^\circ$), the phosphorus atoms occupy equatorial positions, hence the greater electrostatic demands of the phosphinidene ligands diminish the axiality. In 2-Dy, the thermal magnetic relaxation proceeds via the second-excited Kramers’ doublet owing to the near-collinearity of the magnetization axes in the ground- and first-excited doublets. The reduced axiality of the first-excited Kramers’ doublet in 3-Dy, combined with different orientations of the main magnetic axes in the ground- and first-excited doublets, explains the weak magnetic blocking in this system.

The field dependence of the magnetization for 2-Dy shows very narrow hysteresis at 1.8 K, however butterfly-shaped hysteresis was found up to 4.4 K for 2-Y$_2$Dy. The properties of undiluted 2-Dy can be explained in terms of the exchange coupling and frustrated ground state, which enable rapid reversal of the magnetic moments on the individual dysprosium sites. The absence of exchange coupling in 2-Y$_2$Dy allows more prominent blocking of the magnetization.

Substantial changes to SMM properties can be achieved using a bottom-up approach in which dysprosium phosphide complexes are converted into their phosphinidene analogues. The general features of the chemistry and the electronic structure suggest that exploring other lanthanides and other unconventional ligands in place of phosphorus should enable further enhancements in the SMM behaviour.

### Methods

**General synthesis considerations.** All manipulations were performed under an atmosphere of dry, oxygen-free argon, using either standard Schlenk techniques or an argon-filled glove box. Toluene and thf, and their deuterated analogues for NMR spectroscopy, were dried by refluxing over potassium and collected by distillation. All solvents were stored over activated 4 Å molecular sieves and freeze-dried before use. Anhydrous rare-earth chlorides (99.99% purity) were purchased from Strem Chemicals. Lithium aluminium hydride, mesitylmagnesium bromide (1.0 M in hexanes), phosphorus(III) chloride, lithium aluminium hydride, mesitylmagnesium bromide (1.0 M in thf) and di-methylcyclopentadiene (90%) were purchased from Sigma-Aldrich. Mesitylphosphine, the sodium salt of methylcyclopentadienide, and rare-earth tris(methylcyclopentadienide) complexes were synthesised according to the literature procedures.46 Elemental analyses were carried out by Mr Stephen Boyer at London Metropolitan University, UK.

**[Cp]$\langle$2-Dy(PH$_2$Mes)$\rangle$ (1-Dy).** A solution of MesPH$_2$ in toluene (0.5 M, 4.0 ml, 2.0 mmol) was added to a solution of [Cp]$\langle$Dy$\rangle$ (0.8 g, 2.0 mmol) in toluene (4 ml) at room temperature, and the reaction mixture was stirred for 1 h. The resulting pale yellow solution was filtered, concentrated and stored at $\sim 30^\circ$ C overnight, which resulted in the formation of 1-Dy as colourless crystals (0.92 g, 83% isolated yield). Elemental analysis, found percentage (calculated per percentage) for 1-Dy: C, 58.62 (58.74); H, 6.28 (6.21).

**[Cp]$\langle$Y(PH$_2$Mes)$\rangle$ (1-Y).** The synthesis of 1-Y was accomplished using the procedure described above for 1-Dy, with the following amounts: MesPH$_2$ (0.5 M, 4.0 ml, 2.0 mmol), [Cp]$\langle$Y$\rangle$ (0.65 g, 2.0 mmol) and toluene (4 ml). 1-Y formed as colourless crystals (0.71 g, 75% isolated yield). Elemental analysis, found percentage (calculated percentage) for 1-Y: C, 67.39 (67.78); H, 7.21 (7.16). $^1$H NMR (benzene-D$_6$, 298.15 K, $\delta$/ppm): 6.65 (s, 2H, mesityl CH); 5.85, 5.72 (m, 12H, 12C).
C₄H₆CH₂): 3.86 (d, 2H, PH₂, nγ = 251 Hz); 2.16 (s, 6H, ortho CH₃); 2.10 (s, 3H, Cp); 2.03 (s, 3H, para CH₃). ³¹P NMR (benzene-D₆, 298.15 K, δ/ppm): -130.80.

[CP₂(Dy)][μ-P(HOMes)]₃-toluene (2-Dy toluene). ᶠBuLi (1.6 M in hexanes, 0.66 ml, 1.06 mmol) was added to a solution of 1-Dy (0.55 g, 1.06 mmol) in toluene (20 ml) at −78 °C, and the reaction mixture was stirred for 1 h. The reaction was then slowly warmed to room temperature overnight, after which time a pale yellow solution and a precipitate had formed. The resulting pale yellow solution was filtered and concentrated, which resulted in the formation of a yellow precipitate. The precipitate was re-dissolved and the solution stored at −30 °C overnight, which resulted in the formation of 2-Dy toluene as colourless crystalline blocks (0.34 g, 63%). Elemental analysis, found percentage (calculated percentage) for 2-Dy toluene: C, 55.63 (55.76); H, 5.83 (5.75).

[(CP₂(YP)(μ-P(HOMes))₃-toluene (2-Y toluene). The synthesis of 2-Y toluene was accomplished using the procedure described above for 2-Dy toluene, with the following amounts: 1-Y (0.059 g, 1.24 mmol), toluene (20 ml) and ᶠBuLi (1.6 M in hexanes, 0.77 ml, 1.24 mmol). 2-Y toluene was isolated as colourless crystalline blocks (0.37 g, 70% based on yttrium). Elemental analysis, found percentage (calculated percentage) for 2-Y toluene: C, 65.16 (65.32); H, 6.82 (6.74). ¹³¹P NMR (toluene-D₆, 298.15 K, δ/ppm): 6.78–6.93 (3H, methyl CH₃); 5.50–6.55 (6S, 2H, CH₂C₃H₇); 3.47–1.61 (4S, overlapping peaks due to CH₃ groups). ³¹P NMR (benzene-D₆, 298.15 K, δ/ppm): -124.28, -145.21 and -142.65.

Li[(thf)₂][μ-P(CP₂(YP)(μ-P(OMes))₃]-tolf (Li[(thf)₂][μ-P(3-Y)])₃]. A solution of 2-Dy toluene (0.38 g, 0.25 mmol) in thf (10 ml) was cooled to −78 °C and ᶠBuLi (1.6 M in hexanes, 0.47 ml, 0.75 mmol) was added drop wise. After stirring at −78 °C for 30 min, the solution was warmed to room temperature over 3 h, after which time an orange colour had developed. The solution was concentrated until a precipitate had formed. The resulting pale yellow solution was sealed before being transferred to the magnetometer. Each magnetic centre was computed, and neighbouring metal ions were computed, with the magnetic exchange interactions in 1-Dy and 2-Dy being described by single molecule exchange parameter. A solution of the Poly_ANISO program. The exchange interaction between the dysprosium ions is considered within the Lines model, while the contribution of the intramolecular dipole–dipole magnetic coupling is accounted for exactly, which is possible that all necessary data are available from the ab initio calculations. The following references refer to the most complete model B2 (full structure with large basis set). Details of the calculations for models A1, A2 and B1 can be obtained from LFC. Each magnetic centre was computed, and neighbouring metal ions were computationally replaced by diamagnetic Li⁺⁺. The active space of the CASSCF method includes the electrons from the last shell spanning the four 4f orbitals of the Ln³⁺ ion. For all calculations, it was justified to use only a limited number of roots, namely 21 sextets, 128 quartet and 130 doublet states. On the basis of the resulting spin-orbital multiplets, the SINGLE_ANISO programme computed the local magnetic properties (g tensors, main magnetic axes, local magnetic susceptibility, crystal-field parameters and so on). The ab initio results for the individual metal single crystals were used to compute the atomic magnetic moment and the magnetic susceptibility of the trimeletic complexes using the POLY_ANISO program. The exchange interaction between the dysprosium ions is considered within the Lines model, while the contribution of the intramolecular dipole–dipole magnetic coupling is accounted for exactly, which is possible that all necessary data are available from the ab initio calculations.

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Author contributions

R.A.L. conceived the experiments. Synthetic and crystallographic work was carried out by T.P., and T.P. and F.T. conducted the magnetic measurements. L.U. and L.F.C. carried out the theoretical analysis. T.P., L.U., D.C., E.I.L.M. and T.P. Analysed the Author contributions. R.A.L. conceived the experiments. Synthetic and crystallographic work was carried out by T.P., and T.P. and F.T. conducted the magnetic measurements. L.U. and L.F.C. carried out the theoretical analysis. T.P., L.U., D.C., E.I.L.M. and T.P. Analysed the experimental and theoretical data. R.A.L., L.U. and F.T. wrote the manuscript.

Additional information

Accession codes. The X-ray crystallographic coordinates for the structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 1032227-1032232. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

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