Rational Electrostatic Design of Easy-Axis Magnetic Anisotropy in a Zn^{II} - Dy^{III} - Zn^{II} Single-Molecule Magnet with High Energy Barrier

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Introduction

Lanthanide coordination compounds have been the subject of extensive research, because of their intriguing magnetic¹ and photophysical properties.² In recent years, they are playing a crucial role in the field of Molecular Magnetism, because of the high prevalence of lanthanide-containing Single-Molecule Magnets (SMMs).^{1a-g} These chemically and physically fascinating nanomagnets show slow relaxation for the reorientation of the magnetization and magnetic hysteresis when the polarizing magnetic field is removed below the blocking temperature (T_B).³ The magnetic bistability (parallel/antiparallel orientation along the polarizing magnetic field) is due to the existence of an energy barrier for the reversal of the magnetization, which at low temperature dominates on the thermal energy. The thermal energy barrier is essentially tied to the magnetic anisotropy of the system. Lanthanide ions are particularly appropriate candidates to construct SMMs due to their strong magnetic anisotropy, which arises from the combination of large magnetic moments, strong spin-orbit coupling and crystal-field effects.^{1a,h} Although the 4f electrons are effectively shielded by 5s and 5p electrons, they experience the effects of the negative charges of the donor atoms of the ligands. If this ligand field stabilizes the sublevels with the largest M_J values, the Ln^{III} ion exhibits easy-axis anisotropy, which is assumed to be of the Ising type. Of particular interest are the Dy^{III} -containing coordination compounds as the ligand field splits the ground $^6H_{15/2}$ multiplet in such a way that usually the $M_J = \pm 15/2$ is the ground Kramers doublet, which ensures large magnetic moment, bistability and easy axis anisotropy when only the ground state is significantly populated.^{1a} In view of this, it is not surprising that most part of the reported

lanthanide-containing SMMs are constructed from Dy^{III} ions, including those having some of the highest blocking temperatures⁴ and energy barriers.⁵ The free ion electron density for the Dy^{III} ion, and more important that of the ground Kramers doublet with $M_J = \pm 15/2$, have an oblate shape.^{1a} This electron density shape is favored by an axial crystal field, where the donor atoms with the largest electron densities are located above and below the equatorial plane, thus minimizing the repulsive interactions between the ligands and f-electrons charge clouds.^{1a,6} As the phenoxo-oxygen donor atoms have larger negative charge than aldehyde-oxygen donor atoms, a good strategy to achieve strong easy-axis anisotropy would be that of placing the phenoxo oxygen atoms in opposite positions of the Dy^{III} ion, the easy-axis of anisotropy lying in the direction defined by the phenoxo-oxygen atoms. This disposition of the phenoxo oxygen atoms could be achieved in 3d-Dy-3d trinuclear complexes with compartmental ligands bearing phenoxo-bridging groups connecting the 3d-and 4f metal ions and terminal aldehyde groups to be coordinated to the Ln^{III} ion. With regard to the 3d metal ion, it would be preferable to use a diamagnetic ion such as Zn^{II} because (i) a paramagnetic ion could create a random transversal field for the Dy^{III} ions which would favour the faster QTM process and mask the slow relaxation process⁷ (ii) a diamagnetic ion would mitigate the intermolecular interactions that favour the fast QTM.^{5,8} In good agreement with this, some experimental results on Zn-Dy^{6,9} and Zn-Dy-Zn¹⁰ have clearly shown that the substitution of a paramagnetic ion by Zn^{II} increases the effective thermal energy barrier. Following this strategy we report here the synthesis, X-ray structure, magnetic properties and theoretical study of the trinuclear complex [ZnCl(μ -L)Dy(μ -L)ClZn][ZnCl₃(CH₃OH)]·3CH₃OH (**1**) (where H₂L = N,N'-dimethyl-N,N'-bis(2-hydroxy-3-formyl-5-bromo-benzyl)ethylenediamine, see ESI). Likewise, we are reporting the magnetostructural properties of the isostructural complex [ZnCl(μ -L)Er(μ -L)ClZn][ZnCl₃(CH₃OH)]·3CH₃OH (**2**) for comparative purposes as the Er^{III} ion, at variance with **1**, possesses a prolate electron density distribution. These compounds were prepared as yellow crystals by the reaction of H₂L with ZnCl₂ and subsequently with Ln(NO₃)₃·5H₂O (Ln^{III} = Dy, Er) in MeOH and using a 2:2:1 molar ratio.

In the following, the molecular structure of **1** will be described as a representative example to illustrate the common structural features of **1** and **2**. The structure of **1** is given in Figure 1 and consists of a non-centrosymmetric trinuclear [ZnCl(μ -L)Dy(μ -L)ClZn]⁺ cations, [ZnCl₃(CH₃OH)]⁻ anions and three crystallization methanol molecules, all of them involved in hydrogen bonds interactions. Within the trinuclear Zn-Dy-Zn cation, two [ZnCl(L)]⁻ units are

coordinated to the central Dy ion through the phenoxo and aldehyde oxygen atoms belonging to the compartmental ligand H₂L (see Figure 1).

Figure 1-Perspective view of complex **1**. Colour code: N = blue, O = red, Zn = pink, Dy = light green, C = grey, Cl = yellow, Br = brown. Hydrogen atoms, the $[\text{ZnCl}_3(\text{CH}_3\text{OH})]^-$ counteranion and methanol molecules have been omitted for the sake of clarity (left). Structure of the ligand (top right). Square-antiprism DyO₈ coordination sphere in **1** (bottom right).

The Dy(III) ion exhibits a DyO₈ coordination sphere, which is formed by four phenoxo and four aldehyde oxygen atoms, with Dy-O bond distances in the ranges of 2.252-2.348 Å and 2.382 and 2.441 Å, respectively. Calculation of the degree of distortion of the DyO₈ coordination polyhedron with respect to an ideal eight-vertex polyhedron using continuous shape measure theory and SHAPE software,¹¹ led to shape measures relative to the square antiprism (SAPR-8), triangular dodecahedron (TDD-8) and biaugmented triangular prism (BTPR-8) with values of 0.927, 2.173 and 2.862, respectively (see Table S1). The shape measures relative to other reference polyhedra are significantly larger and therefore the DyO₈ coordination polyhedron can be considered as intermediate between the above indicate ideal polyhedra but closer to SAPR-8. The distorted square-antiprism is compressed as the average distance between the upper and lower planes containing the four oxygen atoms (two phenoxo and two aldehyde) is 2.61 Å, whereas the average distance of the side of the squares defined by the oxygen atoms in each plane is 2.77 Å. Zn(II) ions exhibit a ZnO₂N₂Cl coordination

environment with a geometry intermediate between square-pyramid (SPY-5), trigonal bipyramid TBPY-5 and vacant octahedron (v-OC5), but closer to SPY-5 with shape measures average values of 0.92, 3.77 and 3.99. In the SPY-5 description, the nitrogen and oxygen atoms occupy the basal positions with Zn-N and Zn-O bonds distances in the ranges 2.099-2.166 Å and 2.037-2.178 Å, respectively, whereas the axial position is occupied by the Cl atom at a higher distance (2.215 and 2.229 Å). The Zn...Dy distances are 3.578 Å and 3.593 Å, whereas the Zn-Dy-Zn angle is 141.7° within the [ZnCl₃(CH₃OH)]⁻ unit, the Zn(II) ion displays a geometry intermediate between vacant trigonal bipyramid and tetrahedral, with Zn-Cl bond distances in the range 2.224-2.261 Å and a Zn-O bond distance of 2.039 Å. Crystallization methanol molecules and the chloride atoms of the [ZnCl₃(CH₃OH)]⁻ anion are linked by hydrogen bonds to form a chain running along the *c* axis (Figure S1). The shortest Dy...Dy distance between neighboring [ZnDyZn]⁺ trinuclear cations is 7.359 Å.

The direct-current (dc) magnetic susceptibility has been measured on a randomly oriented polycrystalline sample of **1** in the 2-300 K temperature range and under an applied magnetic field of 0.1 T (Figure 2). The $\chi_M T$ value of 13.97 cm³ K mol⁻¹ at 300 K for **1** is compatible with the calculated value of 14.17 cm³ K mol⁻¹ for the ground state of the Dy^{III} ion (4f⁹, $J = 15/2$, $S = 5/2$, $L = 5$, $g = 4/3$ ⁶H_{15/2}) in the free-ion approximation. On cooling, the $\chi_M T$ product decreases monotonically to a value of 11.65 cm³ K mol⁻¹ at 4 K. Below this temperature, there is a change of curvature and $\chi_M T$ decreases more abruptly, reaching a value of 11.36 cm³ K mol⁻¹. This behavior is due to the depopulation of the M_J sublevels of the dysprosium ion, which arise from the splitting of the ⁶H_{15/2} ground term by the ligand field and/or possible very weak intermolecular interaction between the Dy^{III} ions, which could be responsible for the sharp decreases in $\chi_M T$ below 4 K. The M versus H plot at 2 K shows a relatively rapid increase in the magnetization, which saturates for magnetic fields larger than 2 T. The saturation value of 5.47 N μ_B is apparently lower than that expected for a Dy^{III} ion ($M_S/N\mu_B = g_J J = 10 N\mu_B$), likely because of crystal-field effects leading to a significant magnetic anisotropy. The value of $\chi_M' T$ (with an alternating field of 3.2 Oe, see below) at its low temperature plateau (at zero and 1000 Oe) of 12.5 cm³mol⁻¹ K agrees well with that expected for randomly oriented crystals of **1** with a $m_J = \pm 15/2$ Ising ground Kramers doublet (12.5 cm³mol⁻¹K).

Figure 2.- Temperature dependence of $\chi_M T$ for **1**. Inset: Molar magnetization versus field for randomly oriented and oriented microcrystals. Solid lines are the *ab initio* calculated curves.

Dynamic ac magnetic susceptibility measurements as a function of the temperature and frequency (Figure 3 and Figures S2-S5) were performed on a microcrystalline powder sample of **1** with the aim of knowing whether or not it exhibits SMM properties.

Figure 3.-Temperature dependence of the molar out-of-phase ac susceptibility (χ_M'') for **1** under zero dc applied field at different frequencies (top). Temperature dependence of the molar out-of-phase ac susceptibility (χ_M'') for **1** at $H_{dc} = 1000$ Oe at different frequencies (inset). Frequency dependence of the molar out-of-phase ac susceptibility (χ_M'') for **1** at $H_{dc} = 0$ at different temperatures (bottom). Solid lines represent the best fit of the experimental data to the generalized Debye model.

As expected from the easy-axis anisotropy of the Dy^{III} ion (see below for *ab initio* calculations), this complex shows frequency dependence of the out-of-phase (χ''_M) under zero external field below 40 K, which can be attributed to the presence of slow relaxation of the magnetization, indicating that **1** functions as a SMM. In the 17 K (200 Hz)-26 K (10000 Hz) range, we observe a peak that overlaps with a tail at low temperature (χ''_M does not go to zero below the maxima but increases up to 2 K). The appearance of this tail clearly indicates the existence of fast quantum tunneling of magnetization. As Dy^{III} is a Kramers ion, at zero field, dipole-dipole and hyperfine interactions should be responsible for the mixing of the two Kramers ground states that allows the zero-field quantum tunneling dynamics of the magnetization. The Cole-Cole diagram for **1** in the temperature range 17-30 K (Figure 4, inset) exhibits semicircular shapes and can be fitted using the generalized Debye model. This fit provides a value for the parameter α , which is related to the width of the distribution of relaxation times, viz., $\alpha = 1$ corresponds to an infinitely wide distribution of relaxation times, whereas $\alpha = 0$ describes a single relaxation process. We obtain that α is in the range 0.47(17 K)-0.09(30 K), thus suggesting the existence of multiple relaxation processes. The relaxation times extracted from the frequency-dependent susceptibility data follow an Arrhenius law with an effective energy barrier for the reversal of the magnetization $U_{\text{eff}} = 97(2) \text{ cm}^{-1}$ and $\tau_0 = 1.4(2) \times 10^{-7} \text{ s}$ (Figure 4). The U_{eff} is somewhat lower than that predicted from the *ab initio* calculations (energy gap between the ground and first excited Kramers doublet, see below), which can be primarily due to the existence of QTM. The relatively large value of τ_0 confirms that QTM remains operative even where the thermal relaxation is prevailing and therefore relaxation of the magnetization in **1** is not a purely thermal activated Orbach process. The Arrhenius plot constructed from the temperatures and frequencies of the maxima observed for the χ''_M signals in Figure 3 leads virtually to the same result, as expected.

Figure 4.—Arrhenius plots for the relaxation times (τ) extracted from the χ_M'' vs f data in zero and 1000 Oe dc fields. Inset: Cole-Cole (Argand) plot in zero dc field.

The QTM can be partly or fully suppressed by application of a small external dc field, often resulting in an increase of the U_{eff} . Thus, when the ac measurements on **1** were performed in the presence of a small external dc field of 1000 Oe (this field was chosen because it induces the slowest relaxation rate, which does not significantly vary until fields as high as 3000 G), the tails at low temperature almost disappear and the high temperature peaks remain roughly at the same temperatures as those observed under zero dc applied field and exhibit similar intensity. The fact that magnetic fields as high as 3000 Oe are not able to fully eliminate the QTM relaxation process suggests that the remaining QTM process is promoted by intermolecular magnetic dipolar interactions. An appropriate manner to try to eliminate the intermolecular interactions and therefore the QTM process would be that of diluting the sample by co-crystallizing **1** with the isostructural diamagnetic complex of Y^{III}. However, all attempts to obtain crystals of the diluted complex have been unsuccessful thus far. The fit of the relaxation times vs $1/T$ data in the 17 K-30 K temperature range to the Arrhenius law (see Figure 4) leads, to a small increase of the thermal energy barrier and a decrease of τ_0 ($U_{\text{eff}} = 103(2)$ cm⁻¹ and $\tau_0 = 1.07(3) \times 10^{-7}$ s). In the above temperature region, the α values extracted from the Cole-Cole plot (Figure S5) are in the 0.12-0.44 range, which points out to the existence of a distribution of the relaxation times. The τ_0 value is still larger than that usually observed for pure thermally activated processes, thus supporting the existence of QTM at such relatively large temperatures.

In order to support the presence of axial anisotropy and to deep insight in the mechanism of the slow magnetic relaxation properties of **1**, we performed electronic calculations based on the CASSCF+RASSI method.^{12,13} This methodology allows for the description of the highly multiconfigurational character (CASSCF step) of the low lying spectrum of Dy^{III} complexes due to the presence of several low energy excited states, associated with the small ligand field splitting that is observed in lanthanide coordination compounds. Spin-orbit coupling effects are included in a second step (RASSI), considering the previously converged CASSCF wavefunctions (technical details of the calculations are described in the Computational Details section).

Table 1.- Calculated energies (cm⁻¹) and g-factors for the eight lowest Kramers doublets.

Doublet	Energy (cm ⁻¹)	g _z	g _y	g _x
1	0.0	19.430	0.001	0.000
2	129.0	16.488	0.075	0.071
3	257.0	13.046	0.381	0.274
4	334.4	9.932	3.412	1.896
5	374.4	3.211	6.757	9.294
6	455.4	13.404	1.061	0.381
7	502.3	16.541	1.420	0.456
8	560.6	19.453	0.134	0.102

Table 1 presents the calculated energies and g factors for the eight lowest Kramers doublets. These states span an energy interval of 560 cm⁻¹, this range is expectable for Dy^{III} complexes^{10,14} and is a consequence of the small orbital splitting associated with ligand field effects. The excitation energy between the ground and second Kramers doublets is 129 cm⁻¹, also in the typical range for Dy^{III} CASSCF+RASSI calculations. The ground doublet state is calculated to be fundamentally pure $m_j = \pm 15/2$ and markedly axial ($g_z = 19.430$), with almost vanishing transversal components of g (that is to say an almost ideal Ising state) in accordance with their zero-field SMM properties.¹⁵ It is worth mentioning that the experimental temperature dependence of the $\chi_M T$ product and the field dependence of the magnetization can be both well reproduced from the energy levels obtained in the *ab initio* calculations (Figure 2, inset), thus supporting the calculated low-lying state energies for **1**. Furthermore, the calculated excitation energies in the CASSCF step are also favorable for a strongly anisotropic magnetic

moment, with an almost two-fold degenerate ground state (first excitation energy 1.7 cm^{-1}) and a higher second excited state (205.7 cm^{-1}). The plotted beta density of the $4f\text{ Dy}^{\text{III}}$ electrons obtained in the CASSCF step for the first three states is represented in Figure 5 (Dy^{III} is $4f^9$ and the 7 alpha electrons give an isotropic spherical electron density). This energy profile favors the mixing of mostly the first two CASSCF states in the ground RASSI wave function resulting in an oblate beta electron density for such state,¹² because only the third state, that is high in energy, has a different electron density shape.

Figure 5: Beta spin density of the Dy^{III} f electrons for the first three spin-free CASSCF states.

Figure 6.-(Left) molecular structure of **1**. Color code: Dy (green); Zn (magenta); Br (brown); Cl (purple); O (red); N (blue); C (gray). Hydrogens are omitted for clarity. The direction of the magnetic moment of the ground state is indicated as a green arrow. (Right) DFT calculated (B3LYP/TZV) electrostatic potential of the coordination environment (only ligands) projected in a sphere located at the Dy position (1 Å radius). Blue regions correspond to low potential (less repulsive) while highly repulsive regions are indicated in red.

The calculated magnetic moment of the ground state (Figure 6) lies between the planes formed by the two Dy-O-Zn-O moieties, roughly collinear with the two shortest Dy-O distances (2.252 Å and 2.258 Å, with 12.7° and 21.8° deviations between the magnetic moment and the Dy-O bond vectors, respectively) and as expected perpendicular to the oblate shape electron density (see Figure 6). This feature highlights the appropriateness of an axially repulsive coordination environment for achieving SMM properties in Dy^{III} compounds, as qualitatively predicted by the oblate-prolate model.^{1a,6} To verify the influence of the ligand potential in the anisotropy of the 4f density of the Dy^{III} cation, we constructed electrostatic potential maps caused by the ligands projected in the Dy^{III} position by means of DFT calculations. In short, the electrostatic potential gives information about the more (red in Figure 6) and less (blue) repulsive regions from the position of the Dy^{III} ion. Hence, the beta electron density of the ground state (mixing of the two first states of Figure 5) is accommodated in the region with less repulsion (green and blue in Figure 6) to reduce electronic repulsion while in the perpendicular direction, the magnetic moment is pointing towards strongest repulsion regions (red in Figure 6) corresponding to the shortest Dy-O bonds. According with these electrostatic arguments, we have also calculated the direction of the anisotropy axes of the Dy^{III}

ions by using the Chilton's method, which consists in assigning the charge of the ligand using a minimal valence bond model and then constructing an electrostatic crystal field potential. Minimization of the electrostatic energy yields the orientation of the magnetic moments, as stated previously by different authors.^{12,16} As expected, the orientation of the anisotropic axes for each Dy^{III} ion using a simple electrostatic approach (Figure S6) compare rather well with that obtained by *ab initio* methods (Figure 6, left).

We have performed magnetization hysteresis loop measurements on a powder sample of **1** at 0.4 and 2 K and different sweeping rates using a micro Hall-effect magnetometer with the aim of studying the magnetization dynamics and to confirm the SMM properties of **1** (Figure 7). This compound exhibits at 2 K butterfly shaped hysteresis loops with a large step near zero field (Figure 5a), which is consistent with the QTM generally found for 4f containing complexes and with the tail that exhibits this compound at low temperature in the χ_M'' vs T plot. As expected for SMM, the coercitivity increases with increasing field sweep rates. The fact that the coercive field at 0.4 K is lower than at 2 K, when the opposite trend is expected, can be ascribed to a reduction of the tunneling due to thermal activations around the tunnel splitting.^{8b}

Figure 7.- Magnetic hysteresis loops for **1** within $-15 < H/\text{kOe} < 15$ at the indicated sweep rates and temperatures.

It is worth mentioning at this point that the isostructural $[\text{ZnCl}(\mu\text{-L})\text{Er}(\mu\text{-L})\text{ClZn}][\text{ZnCl}_3(\text{CH}_3\text{OH})]\cdot 3\text{CH}_3\text{OH}$ complex (**2**), only exhibits a slight frequency dependence the out-of-phase (χ_M'') signals below ~ 6 K under zero field but without reaching a neat maximum above 2 K even at frequencies as high as 10000 Hz. The lack of a maximum in χ_M'' vs T plot for **2**, points to either the existence of a fast quantum tunneling of the magnetization (QTM) or an energy barrier for the flipping of the magnetization that is not high enough to block the magnetization above 2 K. However, under a 1000 Oe applied dc field the QTM is

almost suppressed and several maxima appear at high frequencies in the 2.2 K (2000 Hz)-3.3 K (10000Hz) range (Figure S7). From the Arrhenius law the effective energy barrier for **2** has been estimated to be 9.3 cm^{-1} with a pre-exponential factor $\tau_0 = 4.5 \times 10^{-7} \text{ s}$. The absence of a significant energy barrier for the reorientation of the magnetization even at $H_{dc} = 1000 \text{ Oe}$ should be due to the lack of easy-axis anisotropy in the ground doublet state, which can be justified using the simple oblate-prolate model. Er^{III} has a prolate electron density distribution and, to avoid the electrostatic repulsion with the negatively charged phenoxo groups, the magnetic moment (and the f-electron cloud) should be located close to the perpendicular to the shorter Dy-O bonds in the mean plane of the aldehyde groups and without a well-defined orientation. This would lead to an easy-plane anisotropy stabilizing a ground state with a low m_j value, which would explain the absence of SMM behavior in **2**. The results obtained for **1** and **2** clearly show the efficacy of the simple oblate-prolate electrostatic repulsion model for predicting SMM behavior in Ln^{III} mononuclear complexes.

The ongoing results represent a clear example of how the simple model based on the prolate-oblate electron density distribution of the Ln^{III} ions can be used to rationally design mononuclear lanthanide-based complexes with strong easy-axis anisotropy and slow relaxation of the magnetization (SMM behavior). Concretely, we have used a compartmental ligand that is able to form Zn-Dy-Zn species, in which the Dy^{III} ion exhibits a DyO_8 coordination environment with slightly distorted axial D_{4d} symmetry. In the DyO_8 coordination sphere, two pairs of large negatively charged phenoxo groups with short Dy-O distances are arranged at opposite sides of the Dy^{III} ion, whereas the remaining position are occupied by neutral aldehyde donor oxygen atoms. The phenoxo donor oxygen atoms exert a strong crystal field and force the oblate electron density to be perpendicular to them in order to minimize electrostatic repulsions. This electrostatic charge distributions would stabilize the strongly axial $m_j = \pm 15/2$ ground Kramers doublet with the anisotropic axis roughly collinear with the shortest Dy-O distances. According to these considerations, experimental magnetic data suggest large easy-axis anisotropy, which is responsible of the high thermal energy barrier for the reversal of the magnetization in zero-field of $U_{\text{eff}} = 140 \text{ K}$ (97 cm^{-1}). *Ab initio* calculations support the easy-axis anisotropy of the ground Kramers doublet, the direction of the anisotropy axis and the thermal activated mechanism for the slow relaxation of the magnetization. The isostructural Zn-Er-Zn species does not present significant SMM behavior as expected for the prolate electron density distribution of the Er^{III} ion.

Experimental section

General Procedures

Unless stated otherwise, all reactions were conducted in oven-dried glassware in aerobic conditions, with the reagents purchased commercially and used without further purification. The ligand H₂L was prepared as previously described.¹⁷

Preparation of complex

[ZnCl(μ-L)Dy(μ-L)ClZn][ZnCl₃(CH₃OH)]·3CH₃OH(1). To a solution of H₂L (64 mg, 0.125 mmol) in 5 mL de MeOH were subsequently added with continuous stirring 17 mg (0.125 mmol) of ZnCl₂ and 27.6 (0.0625 mmol) of Dy(NO₃)₃·5H₂O. The resulting yellow solution was filtered and allowed to stand at room temperature. After one week of attending at room temperature, well formed plate yellow crystals of **1** were obtained with a yield of 45% based on Zn. Anal. Calcd. for C₄₄H₅₆N₄O₁₂Cl₅Br₄Zn₃Dy: C, 31.30; H, 3.34; N, 3.32. C, 31.39; H, 3.39, N, 3.40. FT-IR (KBr) cm⁻¹: 3043 (w), 2920 (w), 1634 (vs), 1585 (s), 1555 (vs), 1295 (vs) 1215 (m), 1035 (m), 947(m).

[ZnCl(μ-L)Dy(μ-L)ClZn][ZnCl₃(CH₃OH)]·3CH₃OH(2). This compound was prepared in a similar manner as for **1** but using Er(NO₃)₃·5H₂O (27.71 mg, 0.0625 mmol) instead of Dy(NO₃)₃·5H₂O with a yield of 41% based on Zn. Anal. Calcd. for C₄₄H₅₆N₄O₁₂Cl₅Br₄Zn₃Er: C, 31.21; H, 3.33; N, 3.31. C, 31.28; H, 3.42, N, 3.21. FT-IR (KBr) cm⁻¹: 3040 (w), 2922 (w), 1635 (vs), 1585 (s), 1551 (vs), 1297 (vs) 1215 (m), 1038 (m), 943(m).

Magnetic Properties: The variable temperature (2-300 K) magnetic susceptibility measurements on a polycrystalline sample of **1** under an applied field of 1000 Oe were carried out with a Quantum Design SQUID MPMS XL-5 device and PPMS 6000. Ac susceptibility measurements under different applied static fields were performed using an oscillating ac field of 3.5 Oe and ac frequencies ranging from 10 to 1000 Hz. The experimental susceptibilities were corrected for the sample holder and diamagnetism of the constituent atoms by using Pascal's tables. A pellet of the sample cut into very small pieces was placed in the sample holder to prevent any torqueing of the microcrystals. Dc magnetic measurements were also carried out with the use of a homemade high-sensitivity micro Hall-effect magnetometer at temperatures down to 0.4 K achieved by a Quantum Design PPMS device. In this case, the grain-like samples consisted of collections of small crystallites of ca. 10⁻³ mm³.

Single-Crystal Structure Determination.

Suitable crystals of **1** and **2** were mounted on a glass fibre and used for data collection. Data for **1** were collected with a Bruker AXS APEX CCD area detector equipped with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) by applying the ω -scan method whereas intensity data for **2** were collected on a Agilent Technologies SuperNovadiffractometer (mirror-monochromated Mo K α radiation, $\lambda = 0.71073$ Å) equipped with Eos CCD detector. Lorentz-polarization and empirical absorption corrections were applied. The structure was solved by direct methods and refined with full-matrix least-squares calculations on F^2 using the program SHELXS97,¹⁸ integrated in WinGX 1.64¹⁹ crystallographic collective package. Anisotropic temperature factors were assigned to all atoms except for the hydrogen atoms, which are riding their parent atoms with an isotropic temperature factor arbitrarily chosen as 1.2 times that of the respective parent. Final $R(F)$, $wR(F^2)$ and goodness of fit agreement factors, details on the data collection and analysis can be found in Table S2. Selected bond lengths and angles are given in Table S3.

CCDC-996361-996362 contains the supplementary crystallographic data (excluding structure factors) of this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details:

Low-energy spectra and g factors of the eight lowest Kramers doublets of **1** were obtained by means of CASSCF+RASSI calculations, as implemented in the MOLCAS 7.8 software package.¹³ The method is divided in two steps: (i) CASSCF(9,7) calculations for three different multiplicities (sextet, quartet and doublet) (ii) The effect of spin-orbit coupling on the basis of the converged wavefunctions obtained in the previous step is included by the Restricted Active Space State Interaction (RASSI) method. Spin Hamiltonian parameters (such as g factors) can be calculated from the wavefunctions resulting after the state interaction step employing the SINGLE_ANISO program. We included 21, 128 and 98 roots for the sextet, quartet and doublet CASSCF calculations, while the employed basis set has the following contractions: Dy[9s8p6d4f3g2h]; Br [4s3p2d1f]; Zn [4s3p2d1f]; Cl [4s3p1d]; O [4s3p2d1f]; N [4s3p2d1f]; C [3s2p]; H [2s]. The structure of the model was extracted from the corresponding X-ray structure without any ligand truncation. Electrostatic potential maps were obtained by DFT calculations (functional: B3LYP, basis: TZVP, program: Gaussian09),²⁰ employing the

geometry for the ligand environment of the previous CASSCF+RASSI calculations and removing the Dy^{III} ion.

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Entry for Table of contents

Two novel Zn-Ln-Zn complexes ($\text{Ln}^{\text{III}} = \text{Dy}, \text{Er}$) have been prepared, where the Ln^{III} ion exhibit an axially distorted square antiprism LnO_8 coordination sphere, with four negatively charged (phenoxo) and four neutral (aldehyde) oxygen atoms. *Ab initio* calculations show that the Dy^{III} ion exhibits high axial anisotropic ground Kramers doublet, the local magnetic moments being almost parallel to the shorter Dy- $\text{O}_{\text{phenoxo}}$ bonds, as predicts the simple electrostatic oblate-prolate model for the oblate Dy^{III} ion. The large energy gap between the ground and first excited doublets of the Dy^{III} ions promotes slow relaxation of the magnetization with a high thermal energy barrier of 140 K. The prolate Er^{III} ion does not show SMM properties according to the easy-plane anisotropy predicted by the electrostatic model.

SUPPORTING INFORMATION

Rational Electrostatic Design of Easy-Axis Magnetic Anisotropy in a Zn^{II} - Dy^{III} - Zn^{II} Single-Molecule Magnet with High Energy Barrier

Itziar Oyarzabal, José Ruiz, José Manuel Seco, Marco Evangelisti, Agustín Camón, Eliseo Ruiz, Daniel Aravena, Enrique Colacio.

Table S1. Continuous Shape Measures Calculations for **1**.

ETBPY-8	13 D3h	Elongated trigonal bipyramid
TT-8	12 Td	Triakis tetrahedron
JSD-8	11 D2d	Snub diphendoid J84
BTPR-8	10 C2v	Biaugmented trigonal prism
JBTPR-8	9 C2v	Biaugmented trigonal prism J50
JETBPY-8	8 D3h	Johnson elongated triangular bipyramid J14
JGBF-8	7 D2d	Johnson gyrobifastigium J26
TDD-8	6 D2d	Triangular dodecahedron
SAPR-8	5 D4d	Square antiprism
CU-8	4 Oh	Cube
HPY-8	3 D6h	Hexagonal bipyramid
HPY-8	2 C7v	Heptagonal pyramid
OP-8	1 D8h	Octagon

Structure [ML8]	ETBPY-8		TT-8		JSD-8
BTPR-8	JBTPR-8	JETBPY-8	JGBF-8	TDD-8	
SAPR-8	CU-8	HBPY-8	HPY-8	OP-8	
Antiprism	,	24.742,	8.029,	5.750,	
2.862,	3.321,	29.125,	15.237,	2.173,	
0.927,	7.165,	13.663,	21.555,	31.300	

Table S2.- Selected crystallographic data for **1**.

Compound	1	2
Formula	C ₄₄ H ₅₆ N ₄ O ₁₂ Cl ₅ Br ₄ Zn ₃ Dy	C ₄₄ H ₅₆ N ₄ O ₁₂ Cl ₅ Br ₄ Zn ₃ Er
<i>M_r</i>	1688.43	1693.30
Crystal system	Orthorhombic	Orthorhombic
Space group (no.)	<i>Pna</i> 21 (33)	<i>Pna</i> 21 (33)

<i>a</i> (Å)	14.343(5)	14.3668(2)
<i>b</i> (Å)	30.712(5)	30.6628(3)
<i>c</i> (Å)	12.898(5)	12.89490(10)
α (°)	90.000(5)	90.000(5)
β (°)	90.000(5)	90.000(5)
γ (°)	90.000(5)	90.000(5)
<i>V</i> (Å ³)	5682(3)	5680.54(11)
<i>Z</i>	4	4
<i>D_c</i> (g cm ⁻³)	1.972	1.977
μ (MoK α) (mm ⁻¹) ^d	5.659	10.020
<i>T</i> (K)	100(2)	100(2)
Observed reflections	9510 (8910)	9943 (9830)
<i>R_{int}</i>	0.0363	0.0218
Parameters	668	659
<i>GOF</i>	1.048	1.063
<i>R₁</i> ^{a,b}	0.0410 (0.0369)	0.0502 (0.0497)
<i>wR₂</i> ^c	0.0841 (0.0822)	0.1360 (0.1356)
Largest difference in peak and hole (e Å ⁻³)	1.606 and -1.060	2.447 and -2.646

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

^b Values in parentheses for reflections with $I > 2\sigma(I)$.

^c $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$

^d In Compound **2** μ (CuK α) (mm⁻¹)^d

Table S3.- Selected bond distances and angles for **1**.

Compound	1	2
Ln(1)-Zn(1)	3.573(1)	3.572(1)
Ln(1)-Zn(2)	3.588(1)	3.562(1)
Ln(1)-O(1A)	2.397(4)	2.366(6)
Ln(1)-O(2A)	2.323(5)	2.327(5)
Ln(1)-O(3A)	2.253(5)	2.231(5)
Ln(1)-O(4A)	2.443(5)	2.409(6)
Ln(1)-O(1B)	2.387(4)	2.383(6)
Ln(1)-O(2B)	2.349(5)	2.303(5)
Ln(1)-O(3B)	2.244(5)	2.248(5)
Ln(1)-O(4B)	2.439(5)	2.418(6)
Zn(1)-N(1A)	2.178(6)	2.159(6)
Zn(1)-N(2A)	2.104(6)	2.108(7)
Zn(1)-O(2A)	2.041(5)	2.071(5)
Zn(1)-O(3A)	2.146(5)	2.166(5)
Zn(1)-Cl(1A)	2.216(2)	2.232(2)
Zn(2)-N(1B)	2.168(6)	2.181(6)
Zn(2)-N(2B)	2.099(6)	2.108(7)
Zn(2)-O(2B)	2.056(5)	2.039(5)

Zn(2)-O(3B)	2.168(5)	2.144(5)
Zn(2)-Cl(1B)	2.223(2)	2.223(2)
Zn(3)-Cl(1C)	2.247(3)	2.252(3)
Zn(3)-Cl(2C)	2.262(3)	2.257(3)
Zn(3)-Cl(3C)	2.227(3)	2.234(4)
Zn(3)-O(1M)	2.02(1)	2.02(1)
Ln(1)-O(2A)-Zn(1)	110.4(3)	108.5(2)
Ln(1)-O(3A)-Zn(1)	108.5(3)	108.6(2)
Ln(1)-O(2B)-Zn(2)	108.9(3)	110.1(2)
Ln(1)-O(3B)-Zn(2)	108.4(3)	108.4(2)
Zn(1)-Ln(1)-Zn(2)	141.47(3)	142.11(3)
O(1A)-Ln(1)-O(2A)	71.8(2)	72.3(2)
O(1A)-Ln(1)-O(4A)	78.0(2)	77.0(2)
O(2A)-Ln(1)-O(3A)	66.9(2)	68.1(2)
O(3A)-Ln(1)-O(4A)	71.5(2)	72.4(2)
O(1B)-Ln(1)-O(2B)	72.2(2)	72.2(2)
O(1B)-Ln(1)-O(4B)	77.0(2)	77.2(2)
O(2B)-Ln(1)-O(3B)	67.7(2)	67.2(2)
O(3B)-Ln(1)-O(4B)	71.9(2)	71.7(2)
O(2A)-Zn(1)-O(3A)	74.2(2)	74.1(2)
O(2A)-Zn(1)-Cl(1A)	111.2(1)	109.4(2)
O(3A)-Zn(1)-Cl(1A)	103.9(1)	102.2(2)
O(2B)-Zn(2)-O(3B)	74.3(2)	73.9(2)
O(2B)-Zn(2)-Cl(1B)	109.5(1)	110.9(2)
O(3B)-Zn(2)-Cl(1B)	101.6(1)	103.9(2)
Cl(1C)-Zn(3)-Cl(2C)	113.3(1)	113.8(1)
Cl(1C)-Zn(3)-Cl(3C)	111.0(1)	111.1(1)
Cl(2C)-Zn(3)-Cl(3C)	122.4(1)	121.8(1)
Cl(1C)-Zn(3)-O(1M)	102.9(4)	103.0(5)
Cl(2C)-Zn(3)-O(1M)	102.4(4)	104.1(5)
Cl(3C)-Zn(3)-O(1M)	101.6(4)	99.8(5)

Figure S1.- Perspective view of the hydrogen bonds chain formed by the $[\text{ZnCl}_3(\text{CH}_3\text{OH})]^-$ anions and crystallization methanol molecules.

Figure S2.-Temperature dependence of the molar in-phase ac susceptibility (χ_M') for **1** under zero dc applied field at different frequencies.

Figure S3.- Temperature dependence of the molar in-phase ac susceptibility (χ_M') for **1** under a 1000 Oe dc applied field at different frequencies.

Figure S4.-Temperature dependence of the molar in-phase ac susceptibility (χ_M'') for **1** under a 1000 Oe *dc* applied field at different frequencies.

Figure S5.- Cole-Cole plot for **1** under a dc field of 1000 Oe.

Figure S6.-(left) Partial Charges assigned to the charged ligands. The rest of the atoms have zero charge. (right) Anisotropy axis for the Dy^{III} ion (red line). The local magnetic moment forms an angle with the shorter Dy-O distances plane of 14.43° and 13.99° , which are close to the direction of that extracted using CASSCF *ab initio* calculations.

Figure S7.- Temperature dependence of the molar in-phase ac susceptibility (χ_M') for **2** under a 1000 Oe *dc* applied field at different frequencies.

Figure S8.- Temperature dependence of the molar out-of-phase ac susceptibility (χ_M'') for **2** under a 1000 Oe dc applied field at different frequencies.

Figure S9.- Cole-Cole plot for **2** under a dc field of 1000 Oe.

Figure S10.- Arrhenius plot for **2** under a *dc* field of 1000 Oe.