Two C₃ symmetric Dy^{III} Complexes with Triple Di-μ-Methoxo-μ-Phenoxo Bridges, Magnetic Ground State and SMM Behaviour

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Abstract: Two series of isostructural C₃ symmetric Ln₃ complexes Ln₃·[BPh₄] and Ln₃·0.33[Ln(NO₃)₆] (where Ln^{III} = Gd and Dy) have been prepared from an amino-bis(phenol) ligand. X-ray studies reveal that Ln^{III} ions are connected by one μ₂-phenoxo and two μ₃-methoxo bridges, leading to a hexagonal bipyramidal Ln₃O₅ bridging core, where Ln^{III} ions exhibit a biaugmented trigonal prismatic geometry. Magnetic susceptibility studies and *ab initio* CASSCF calculations indicate that the magnetic coupling between the Dy^{III} ions, which possess a high axial anisotropy in the

ground state, is very weak antiferromagnetic and mainly dipolar in nature. To reduce the electronic repulsion from the coordinating oxygen atom with the shortest Dy-O distance, the local magnetic moments are oriented almost perpendicular to the Dy₃ plane leading to a paramagnetic ground state. CASSCF+RASSI calculations also show that the ground and first excited state of the Dy^{III} ions are separated by ~150 cm⁻¹ and ~177 cm⁻¹, for Dy₃·[BPh₄] and Dy₃·0.33[Dy(NO₃)₆], respectively. As expected for these large energy gaps, Dy₃·[BPh₄] and Dy₃·0.33[Dy(NO₃)₆]

exhibit, under zero *dc* field, thermally activated slow relaxation of the magnetization, which overlap with a quantum tunneling relaxation process. Under an applied *H_{dc}* field of 1000 Oe, Dy₃·[BPh₄] exhibits two thermally activated processes with *U_{eff}* values of 34.7 cm⁻¹ and 19.5 cm⁻¹, whereas Dy₃·0.33[Dy(NO₃)₆] shows only one activated process with *U_{eff}* = 19.5 cm⁻¹.

Keywords: Single-molecule magnets • Triangular lanthanide complexes • Dysprosium • Magnetic Properties • Ab initio calculations

Introduction

Single-Molecule Magnets (SMMs) are molecular entities that can function as single-domain nanoparticles, exhibiting slow relaxation of the magnetization and magnetic hysteresis below the so-called blocking temperature (*T_B*).^{1,2} These chemically and physically fascinating nanomagnets have been suggested for applications in molecular spintronics, ultra-high density magnetic information storage³ and quantum computing at molecular level.⁴ The ultimate goal of the enormous research activity in the field of SMMs is the prospect of integrating them in nanosized devices.⁵

The origin of the SMM behaviour is the existence of an energy barrier (*U*) that prevents reversal of the molecular magnetization when the external field is removed, leading to bistability of the ground state.¹ However, most currently observed energy barriers are low and therefore SMMs act as magnets only at very low temperatures. To increase the height of the energy barrier and therefore to improve the SMM properties, systems with large spin-ground states and/or with large magnetic anisotropy are required. Recently, researchers have focused their attention to complexes containing lanthanide (and actinide) cations.⁶ In Ln^{III} ions, the *f* electrons are very efficiently shielded by the fully occupied 5s and 5p orbitals and therefore interact faintly with the ligand electrons. Consequently, the ligand effects are very weak and most of the Ln^{III} complexes exhibit large and unquenched orbital angular momentum. Hence, the Ln^{III} complexes in general exhibit large intrinsic magnetic anisotropy and large magnetic moments, which can lead to higher energy barriers and thus to improved SMM properties.⁶

Mixed metal 3d/4f aggregates^{2,7} and low-nuclearity 4f metal complexes^{6,8} have been reported to exhibit slow relaxation of the magnetization with *U* and *T_B* values as high as 652 cm⁻¹ and 14 K, respectively.^{9,10} Among series of lanthanide cluster reported to date, Dy₃ triangles have gained considerable amount of attention because of the observed slow relaxation of the magnetization despite their non-magnetic ground state. Experimental¹¹ and theoretical studies¹² demonstrated that this is due to the non-collinearity of the planar easy anisotropy axis of the Dy^{III}-ions, leading to a toroidal

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alignment of the local magnetization vectors. This toroidal distribution can be regarded as a form of vortex spin chirality, as there exist two opposite rotations of the magnetization vectors and to convert one into the other, it is necessary to overcome an energy barrier. The chiral nature of the distribution of magnetization vectors in triangular Dy_3 complexes may open new perspectives in molecular spintronics and qubits.^{6d,13}

In view of the exceptional magnetic of the preceding complexes, great efforts have been dedicated in recent years to design and prepare more examples of Dy_3 triangles with the aim of analysing the structural features affecting the relaxation dynamics in this type of system, as some of the triangular Dy_3 species do not show non-magnetic ground state at low temperatures.^{11e} Furthermore, one of the reported Dy_3 complexes was shown to act as a multiferroic system combining SMM behaviour and ferroelectricity.^{9e} It has been also shown that the linking two Dy_3 triangles through hydrogen bonds increases the thermal energy barrier up to values as high as 139 cm^{-1} ,¹⁴ whereas their antiferromagnetic linkage through a chiral paramagnetic copper(II) complex has been shown to afford multiferroic 1D systems.¹⁵ All the above results demonstrate the vast potential of the Dy_3 complexes in the preparation of novel multifunctional materials.

Scheme 1. Structure of the H_2L ligand (left) and its coordination mode in the Dy_3 complexes.

Herein, we report the synthesis, X-ray structures, detailed dc/ac magnetic studies and theoretical calculations of two new cationic dysprosium triangles $[\text{Dy}_3(\text{L})(\mu_3\text{-OMe})_2(\text{NO}_3)_3](\text{Dy}_3)$ with two different anions ($\text{Dy}_3\cdot[\text{BPh}_4]$ and $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$) using a multidentate amino-bis(phenolate) ligand (H_2L , Scheme 1) which provides up to seven possible donor atoms thus enabling it to coordinate to metal cations in several different coordination modes. The fact that the ligand exhibits neighbouring hydroxy and methoxy groups in the phenyl rings favours the coordination of the oxophilic Dy^{III} ions, whereas the deprotonation of the hydroxy group can allow the formation of phenoxo-bridged polynuclear species.

Results and Discussion

The complexes $\text{Dy}_3\cdot[\text{BPh}_4]$ and $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$, as well as their Gd-counterparts, were synthesized as air and moisture stable compounds with excellent to reasonable yields in ambient laboratory atmosphere. The reaction of H_2L with either $\text{Ln}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ ($\text{Ln}^{\text{III}} = \text{Dy}, \text{Gd}$) and subsequently with NaBPh_4 and triethylamine in MeOH and using a 1:1:0.5:2 molar ratio led to colourless crystals of the compounds $\text{Ln}_3\cdot[\text{BPh}_4]$ in very good yield. In the absence of NaBPh_4 and using a $\text{H}_2\text{L}/\text{Ln}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}/\text{triethylamine}$ 1:1.33:2 molar ratio, the reaction led to colourless crystals of $\text{Ln}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ in moderate yield.

The magnetically most interesting Dy^{III} containing compounds are used as examples to describe molecular structures of complexes.

The structure of $\text{Dy}_3\cdot[\text{BPh}_4]$ consists of a mono-cationic equilateral triangular $[\text{Dy}_3]^+$ unit and a tetraphenyl borate anion, while in complex $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ the $[\text{BPh}_4]^-$ anion has been replaced by the $[\text{Dy}(\text{NO}_3)_6]^{3-}$ anion with occupation of 0.66 per atom in each site. The partially occupied $[\text{Dy}(\text{NO}_3)_6]^{3-}$ anions and complete $[\text{Dy}_3]^+$ cations occur in structure in 1:2 ratio, thus, balancing the total charge of the compound. Both structures contain non-coordinated, disordered solvent molecules (methanol and water) which fill the cavities in the lattice. Although $\text{Dy}_3\cdot[\text{BPh}_4]$ and $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ crystallize in different space groups of the trigonal system, $P\bar{3}$ and $R\bar{3}$, respectively, they exhibit the same $[\text{Dy}_3]^+$ cationic units with small differences affecting bond distances and angles (see Figure 1 and Table 1).

Figure 1. The basic cationic structural unit and atomic labelling scheme for $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ is given as an example. Symmetry operations: $' = 2-x+y, 1-x, z$; $'' = 1-y, -1-x-y, z$. (Left). Biaugmented trigonal prism geometry of the Dy^{III} coordination polyhedron (right).

Table 1. Selected bond lengths (Å) and angles ($^\circ$) around Dy^{III} ion of $\text{Dy}_3\cdot[\text{BPh}_4]$, $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$, $\text{Gd}_3\cdot[\text{BPh}_4]$ and $\text{Gd}_3\cdot 0.33[\text{Gd}(\text{NO}_3)_6]$.

	$\text{Dy}_3\cdot[\text{BPh}_4]$	$\text{Dy}_3\cdot 0.33$	$\text{Gd}_3\cdot[\text{BPh}_4]$	$\text{Gd}_3\cdot 0.33$
		$[\text{Dy}(\text{NO}_3)_6]$		$[\text{Gd}(\text{NO}_3)_6]$
Ln1-Dy1'	3.5425(7)	3.5251(7)	3.5936(8)	3.8542(9)
Ln1-O1	2.429(7)	2.437(4)	2.451(8)	2.473(5)
Ln1-O1'	2.337(7)	2.326(6)	2.37(1)	2.361(8)
Ln1-O2	2.182(7)	2.194(6)	2.196(9)	2.234(6)
Ln1-O3'	2.567(7)	2.601(6)	2.586(8)	2.615(7)
Ln1-O4	2.982(8)	3.010(8)	2.908(8)	2.953(5)
Ln1-O5	2.382(5)	2.382(5)	2.405(6)	2.408(5)
Ln1-O6	2.368(4)	2.341(4)	2.385(5)	2.389(5)
Ln1-O7	2.455(5)	2.477(6)	2.49(1)	2.489(8)
Ln1-O8	2.472(4)	2.468(8)	2.508(8)	2.499(7)
Ln2-O10	-	2.51(1)	-	2.57(1)
Ln2-O11	-	2.554(8)	-	2.560(9)
Ln1-O1-Ln1'	96.0(2)	95.4(2)	96.4(3)	95.7(2)
Ln1-O5-Ln1'	96.0(3)	95.5(3)	96.7(4)	96.2(3)
Ln1-O6-Ln1'	96.9(3)	97.7(3)	97.8(4)	97.2(3)

Within the $[\text{Dy}_3]^+$ unit, the Dy_3 equilateral triangle is capped, above and below the plane defined by the Dy^{III} ions, with two monoanionic μ_3 -methoxo groups lying on the three-fold axis passing through the triangle barycentre. Each pairs of Dy^{III} -ion are additionally bridged by one phenolate group belonging to one of the three mono deprotonated amino-bis(phenol) ligands present in the structure, giving rise to a hexagonal bipyramidal Dy_3O_5 bridging core with the axis of the bipyramid passing through the O5 and O6 oxygen atoms belonging to the μ_3 -OMe bridging ligands. The other phenolate group of each ligand is terminally coordinated to the corresponding Dy^{III} ion leading to a *cis*-conformation for the ligand (see Scheme 1 for the coordination mode of the ligand). The amino nitrogen atom between the aromatic rings is protonated, hence the ligand acts in a zwitterionic form and causes the effective charge of the ligand moiety to be only -1. The triangle retains C_3 -symmetry making all Dy^{III} -ions structurally and magnetically equivalent. Remaining coordination sites are occupied by bidentately bound nitrate anions and aromatic methoxy substituents creating 8-coordination for all lanthanide ions. The calculation of the degree of distortion of the DyO_8 coordination polyhedron inside the Dy_3 triangle with respect to an ideal eight-vertex polyhedra, by using the continuous shape measure theory and SHAPE software,¹⁶ indicated that in both compounds the DyO_8 arrangement is intermediate between various coordination polyhedra (see Tables S1 and S2). Nevertheless, the shape measures relative to ideal biaugmented trigonal prism are by far the lower ones with values of 1.59 for $\text{Dy}_3\cdot[\text{BPh}_4]$ and 1.43 for $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ (see Figure 1). The DyO_{12} coordination environment in the $[\text{Dy}(\text{NO}_3)_6]^{3-}$ anion of $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ exhibits a distorted icosahedral geometry (see Figure S1). The morpholine groups of the ligand HL^- are all

arranged perpendicularly to Dy_3 plane forming a cup-like conformation for the whole cation. The formed cup is filled with either disordered phenyl group from the anion ($\text{Dy}_3\cdot[\text{BPh}_4]$) or with disordered methanol molecule ($\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$) (Figure S2).

Figure 2. Intramolecular hydrogen bonding in the Dy_3 triangle.

Selected bond lengths and angles in the Dy_3O_5 bridging core are in agreement with those found for similar complexes reported earlier. The differences in these parameters between the structures with different anions are minor with most notable variation in the bridging angles between the Dy^{III} ions. To the best of our knowledge, the compounds reported herein are only the second examples of equilateral triangular Dy_3 systems with μ_3 -methoxo bridging groups (see Table 2).

Table 2. Magneto-structural data for triangular Dy_3 SMMs.

Complex	U_{eff} (cm^{-1})	Coordination Polyhedron	Geometry ^c	Internal bridges	Ground State	Ref
$[\text{Dy}_3(\mu_3\text{-OH})_2\text{L}_3\text{Cl}_2(\text{H}_2\text{O})_4][\text{Dy}_3(\mu_3\text{-OH})_2\text{L}_3\text{Cl}(\text{H}_2\text{O})_5]\text{Cl}_5\cdot 19\text{H}_2\text{O}$	25	2DyO_8 $\text{DyO}_7\text{Cl}^{\text{a}}$ $\text{DyO}_6\text{Cl}_2^{\text{a}}$	d	$\mu_3\text{-OH}$	NM (AF)	11a
$[\text{Dy}_3(\mu_3\text{-OH})_2\text{L}_3\text{Cl}(\text{H}_2\text{O})_5]\text{Cl}_3\cdot 4\text{H}_2\text{O}\cdot 2\text{MeOH}\cdot 0.7\text{MeCN}$	42.9	2DyO_8 DyO_7Cl	d	$\mu_3\text{-OH}$	NM(AF)	11a
$[\text{Dy}_3(\mu_3\text{OH})_2(\text{H}p\text{ovh})_3(\text{NO}_3)_3(\text{MeOH})_2(\text{H}_2\text{O})]\text{NO}_3\cdot 3\text{CH}_3\text{OH}\cdot 2\text{H}_2\text{O}$	37.4 4.2	DyO_9	CSAPR-9	$\mu_3\text{-OH}$	NM(AF)	11b
$[\text{Dy}_3(\mu_3\text{OH})_2(\text{H}_2\text{vovh})_3\text{Cl}_2(\text{CH}_3\text{OH})(\text{H}_2\text{O})_3][\text{Dy}_3(\mu_3\text{OH})_2(\text{H}_2\text{vovh})_3\text{Cl}_2(\text{H}_2\text{O})_4]\cdot \text{Cl}_4\cdot 2\text{CH}_3\text{OH}\cdot 2\text{CH}_3\text{CN}\cdot 7\text{H}_2\text{O}$	15.1 ^c 57.1 ^c	DyO_8 $2\text{DyO}_7\text{Cl}$	d	$\mu_3\text{-OH}$	NM(AF)	11b
$\text{Dy}_3(\text{HL})(\text{H}_2\text{L}^1)(\text{NO}_3)_4$	63.1 29.6	DyO_8 $2\text{DyO}_7\text{N}_2$	SAPR-8 CSAPR-9	$\mu_3\text{-OR}$	NM(AF)	11c
$[\text{Dy}_3(\text{L}^2)(\mu_3\text{OH})_2(\text{NO}_3)_2(\text{H}_2\text{O})_4]\cdot 2\text{NO}_3\cdot 6\text{MeOH}\cdot \text{H}_2\text{O}$	~0.35	$3\text{DyO}_6\text{N}_2$	TDD-8	$\mu_3\text{-OH}$	M(F)	11d
$[\text{Dy}_3(\text{L}^2)(\mu_3\text{OH})_2(\text{SCN})_4(\text{H}_2\text{O})_2]\cdot 3\text{MeOH}\cdot 2\text{H}_2\text{O}$	11.1 ^b	$3\text{DyO}_5\text{N}_3$	TDD-8	$\mu_3\text{-OH}$	M(F)	11d
$[\text{Dy}_3(\mu_3\text{-OCH}_3)_2(\text{HL}^3)_3(\text{SCN})]\cdot 4\text{CH}_3\text{OH}\cdot 2\text{CH}_3\text{CN}\cdot 2\text{H}_2\text{O}$	6.2 3.1	$2\text{DyO}_6\text{N}_2$ $2\text{DyO}_6\text{N}_3$	BTPR-8 TCTPR-9	$\mu_3\text{-OCH}_3$	M (U)	11e
$[\text{Dy}_3(\mu_3\text{-N}_3)(\mu_3\text{-OH})(\text{H}_2\text{L}^3)_3(\text{SCN})_3](\text{SCN})\cdot 3\text{CH}_3\text{OH}\cdot \text{H}_2\text{O}$	~2	$3\text{DyO}_5\text{N}_4$	TCTPR-9	$\mu_3\text{-OH}$ $\mu_3\text{-N}_3$	M(U)	11e
$\text{Dy}_3\cdot [\text{BPh}_4]$	34.7 ^c 19.5 ^c	DyO_8	BTPR-8	$\mu_3\text{-OCH}_3$	M(AF)	This work
$\text{Dy}_3\cdot [\text{Dy}(\text{NO}_3)_6]$	19.5 ^c	DyO_8	BTPR-8	$\mu_3\text{-OCH}_3$	M(AF)	This work

^a50:50 disorder ^bWith a dc applied field of 500 Oe. ^cWith a dc applied field of 1000 Oe ^d Pentagonal bipyramid where one site in the pentagonal plane has been replaced by two μ -hydroxo sites above and below it. HL = o-vanillin; H₂povh = N-(pyridylmethylene)-o-vanilloylhydrazone; H₂vovh = N-vanillidene-O-vanilloylhydrazone; H₄L¹ = N,N,N,N-tetrakis(2-hydroxyethyl)-ethylene-diamine. H₃L² = trinucleatingnonadentate NaO_3 ligand. H₃L³ = 2,6-diformyl-4-methylphenoldi(benzoylhydrazone). ^e All geometries are distorted. CSAPR-9 = Capped square antiprism; SAPR-8 = Square antiprism; TDD-8 = Trigonal Dodecahedron; BTPR-8 = Bicapped trigonal prism; TCTPR-9 = tricapped trigonal prism. NM = non-magnetic. M = magnetic. AF = antiferromagnetic coupling. F = ferromagnetic coupling. U = unknown

Shortest intertriangle Dy...Dy distances are over 10 Å, whereas the shortest intermolecular Dy...Dy separations between cation and anion in **Dy₃·0.33[Dy(NO₃)₆]** are ~ 11 Å. The intermolecular hydrogen bonds do not play any key role in the packing of the complexes although some of the disordered water/methanol molecules seem to form hydrogen bonding networks around the anion in **Dy₃·0.33[Dy(NO₃)₆]**. Nevertheless, it should be noted that the solid state structures of both compounds contain fair amount of weak interactions between the heteroatom polarized methylene/aromatic CH-hydrogens and certain acceptor atoms (oxygen and nitrogen) of the counter-anions, solvents of crystallization or neighbouring triangles. Conversely, the conformation of the ligands around the Dy₃-triangle is almost solely determined by the strong intramolecular R₃NH...OR H-bonds (Figure 2).

Magnetic Properties

The direct-current (dc) magnetic susceptibility of **Dy₃·[BPh₄]** and **Dy₃·0.33[Dy(NO₃)₆]** have been measured in the 2-300 K temperature range under an applied magnetic field of 0.1 T and using a divided pellet, which was made from a microcrystalline powder sample of the compounds, to prevent any torqueing of the magnetically anisotropic sample (Figure 3).

Figure 3. Temperature dependence of the $\chi_M T$ product for **Dy₃·[BPh₄]** (left) and **Dy₃·0.33[Dy(NO₃)₆]** (right). Inset: Field dependence of the magnetization. The black solid lines represent the *ab initio* calculated curves.

The room temperature $\chi_M T$ value for **Dy₃·[BPh₄]** and **Dy₃·0.33[Dy(NO₃)₆]** of 42.4 cm³ K mol⁻¹ and 47.6 cm³ K mol⁻¹ at 300 K are compatible with the calculated values of 42.51 cm³ K mol⁻¹ and 47.2 cm³ K mol⁻¹ for three and three and half non-coupled Dy^{III} ions (4f⁹, $J = 15/2$, $S = 5/2$, $L = 5$, $g = 4/3$ ⁶H_{15/2}), respectively, in the free-ion approximation. On cooling, the $\chi_M T$ product steadily decreases to ~ 25 K and then drops sharply to reach value of 19.99 cm³ K mol⁻¹ and 21.65 cm³ K at 2 K for **Dy₃·[BPh₄]** and **Dy₃·0.33[Dy(NO₃)₆]**, respectively. This behaviour is due to the depopulation of the excited m_j sublevels of dysprosium ions, which arise from the splitting of the ⁶H_{15/2} ground term by the ligand field, and/or possible very weak intra/intermolecular interactions between the Dy^{III} ions. As Dy^{III} and Gd^{III} generally exhibit the same type of magnetic exchange interaction (ferromagnetic or antiferromagnetic) in isostructural compounds, we have prepared the isostructural complexes **Gd₃·[BPh₄]** and **Gd₃·0.33[Gd(NO₃)₆]** with the aim of knowing if **Dy₃·[BPh₄]** and **Dy₃·0.33[Dy(NO₃)₆]** present antiferromagnetic interaction between the Dy^{III} ions. The magnetic properties of the complexes **Gd₃·[BPh₄]** and **Gd₃·0.33[Dy(NO₃)₆]** are given in Figures S3 and S4 in the form $\chi_M T$ vs T , together with their M vs T plots. At room temperature, the $\chi_M T$

values for **Gd₃·[BPh₄]** and **Gd₃·0.33[Gd(NO₃)₆]** of 25.25 cm³ K mol⁻¹ and 26.80 cm³ K mol⁻¹, respectively, are in good agreement with those expected for three and three and half uncoupled Gd^{III} ions of 25.30 cm³ K mol⁻¹ ($S = 7/2$ and $g = 2.07$) and 26.75 cm³ K mol⁻¹ ($S = 7/2$ and $g = 2.07$), respectively. On lowering temperature, the $\chi_M T$ products for **Gd₃·[BPh₄]** and **Gd₃·0.33[Gd(NO₃)₆]** remain constant until ~ 35 K and then decreases abruptly to reach values of 9.8 cm³ K mol⁻¹ and 12.5 cm³ K mol⁻¹ at 2 K, respectively. As the Gd^{III} ions present no spin-orbit coupling at the first order, the decrease of the $\chi_M T$ at low temperature points out directly to the presence of a very weak antiferromagnetic interaction between the Gd^{III} ions and/or zero-field splitting (ZFS) effects of the Gd^{III} ions. The field dependence of the magnetization at 2 K for **Gd₃·[BPh₄]** and **Gd₃·0.33[Gd(NO₃)₆]** (Figures S3 and S4 inset), show that the experimental magnetization values are well below the Brillouin function for three Gd^{III} ions, which supports the antiferromagnetic interaction and/or ZFS in this complex. At high field the saturation of the magnetization is almost complete at 5 T, reaching values of 21.27 N_{μ_B} and 22.96 N_{μ_B} **Gd₃·[BPh₄]** and **Gd₃·0.33[Gd(NO₃)₆]**, respectively, which agrees well with the theoretical saturation value for three and three and half Gd^{III} ions of 21.7 (for $g = 2.07$) N_{μ_B} and 23.56 N_{μ_B} (for $g = 2.02$), respectively.

The magnetic susceptibility data of **Gd₃·[BPh₄]** and **Gd₃·0.33[Dy(NO₃)₆]** were modelled with the following Hamiltonian:

$$H = -J (S_{Gd1}S_{Gd2} + S_{Gd2}S_{Gd3} + S_{Gd1}S_{Gd3}) \quad (1)$$

The fit of the experimental susceptibility data with the above Hamiltonian using the full-matrix diagonalization MAGPACK program¹⁷ afforded the following set of parameters: $J = -0.16$ cm⁻¹ and $g = 2.07$ for **Gd₃·[BPh₄]**, $J = -0.17$ cm⁻¹ and $g = 2.02$ for **Gd₃·0.33[Dy(NO₃)₆]**. The experimental magnetization data are very well reproduced with these best fit parameters (see inset Figures S3 and S4). Although the obtained values are in good agreement with the reported coupling constants for phenoxo-bridged Gd^{III} complexes¹⁸ they should be taken with caution because the possible existence of ZFS splitting of the Gd^{III} ions. Therefore, the above J values can be considered as the upper limit for the antiferromagnetic magnetic exchange interaction between the Dy^{III} ions (for negligible ZFS effects). The extracted J values agree rather well with the DFT calculated values of -0.217 cm⁻¹ and -0.226 cm⁻¹ for **Gd₃·[BPh₄]** and **Gd₃·0.33[Dy(NO₃)₆]**, respectively.

In order to study the nature of the magnetic exchange interaction between the Dy^{III} ions inside the [Dy₃]⁺ unit and to determine the relative orientation of the main anisotropy axes, *ab initio* fragment CASSCF calculations were performed within the MOLCAS 7.8 package (see Supporting Information for details). These calculations show the splitting of the ⁶H_{15/2} ground atomic term into eight Kramers' doublets, the first excited Kramers' doublets being separated from the ground ones by the energies (U_{cal} assuming spin relaxation through the first excited state) given in Table 3. The large energy gap between the ground and first excited state, that would correspond to the thermal energy barrier for the Dy^{III} ions inside the [Dy₃]⁺ unit, is not unexpected in view of the biaugmented trigonal prismatic geometry of their corresponding DyO₈ coordination polyhedral.¹⁹ The relatively small separations in the calculated energy spectrum of the Dy^{III} ion in the [Dy(NO₃)₆]³⁻ are not unexpected as the distorted icosahedral geometry of the DyO₁₂ coordination polyhedron shows a quasi-spherical ligand electrostatic field. Moreover, the ground Kramers' doublets have

strong axial anisotropy with very small transverse components along the main anisotropy axes (see Table 3). The magnetic interaction within the $[\text{Dy}_3]^+$ are sum of the dipolar and exchange interactions. The former one were calculated from the g tensors in the ground state of the Dy^{III} fragments, whereas the latter ones were extracted from the simultaneous fitting of the temperature dependence of susceptibility and the field dependence of the field within the Lines model²⁰ (see Figure 3 and 4). In this approach, a single coupling constant for every interacting pair represents the magnetic coupling between centres while the local anisotropy of the Dy^{III} is represented in the site basis, which is constructed from the wavefunctions obtained after the inclusion of spin-spin orbit effects in the CASSCF+RASSI calculation. The obtained J values (sum of dipolar and magnetic exchange interactions) are also given in Table 3.

Table 3. Calculated values for the CASSCF+RASSI first excitation energy, (U_{cal}), g tensors for the ground doublet state of the Dy^{III} ion and $J_{\text{Dy-Dy}}$ intra-triangle magnetic exchange coupling for the model compounds.

	$\text{Dy}_3\cdot[\text{BPh}_4]$	$\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$	$[\text{Dy}(\text{NO}_3)_6]^+$
$U_{\text{cal}} (\text{cm}^{-1})$	149.9	177.2	36.5
g_x	0.061	0.060	0.049
g_y	0.103	0.106	0.073
g_z	19.616	19.592	15.253
$J (\text{cm}^{-1})$	-0.213	-0.225	-
dipolar+exchange			
$J (\text{cm}^{-1})$ exchange	-0.006	-0.019	-

The major contribution for the antiferromagnetic interaction comes from the magnetic dipolar coupling rather than from exchange, a similar behaviour was previously observed in a binuclear Ho^{III} complex.²¹ In the case of $\text{Dy}_3\cdot[\text{BPh}_4]$ and $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$, the relatively high angle between the local magnetic moments of the ground state and the molecular plane (70° and 72°) (see Figure 4) determines the negative sign of the magnetic dipolar interaction, that is governed by the following equation:²²

$$E_{dp} = - \left\{ \frac{\mu_0}{4\pi} \right\} \frac{1}{r_{ij}^3} \left[3(\vec{\mu}_i \cdot \vec{u}_{ij})\vec{u}_{ij} - \vec{\mu}_i \right] \cdot \vec{\mu}_j \quad (2)$$

Where u_{ij} is the unit vector connecting the position of the interacting centres and r is their distance, $\mu_{i,j}$ are the magnetic moments of centers i and j and μ_0 is the vacuum permittivity. This expression leads to antiferromagnetic coupling for angles between the magnetic moments and the molecular plane bigger than 58.2° and ferromagnetic coupling for angles lower than 58.2° , respectively (for an angle value of 33.6° between the magnetic moments i and j , while the threshold angle value for a collinear system is 54.7°).

Due to the large anisotropy for these systems, the local magnetic moments of the Dy^{III} ions are almost perpendicular the plane of the $[\text{Dy}_3]^+$ triangles and the local magnetic moments form an angle with the Dy_3 plane of 70° and 72° , for $\text{Dy}_3\cdot[\text{BPh}_4]$ and $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$, respectively (see Figure 4). The orientation of the magnetic moments can be easily understood due to the presence of the shortest Dy-O distance (O2 in Table 1 and green oxygen atom depicted in Figure 4). The f electron density of the $m_j = 15/2$ Dy^{III} centres has an oblate shape.^{6a} Thus, in order to reduce the repulsion with the closest coordinated atom, the electron density disc is accommodated almost perpendicular to the shortest Dy-O bond.²³

Hence, the resulting magnetic moment is perpendicular to the electron density disc and consequently, in the direction of the shortest Dy-O bond (see Fig. 4). We have calculated the direction of the anisotropy axes of the Dy^{III} ions by using a simple electrostatic model recently reported by Chilton *et al.* This method consists in assigning the charge of the ligand using a minimal valence bond model and then to construct an electrostatic crystal field potential. Minimization of the electrostatic energy yields the orientation of the magnetic moments.²⁴ As it can be observed in Figure S8, the orientation of the anisotropic axis on each Dy^{3+} ion compare rather well with that obtained by *ab initio* methods (see Fig. 4). As a consequence of this orientation, the magnetization vectors of the ground Kramers' doublets do not compensate each other and the ground state, at variance with other previously reported Dy_3 triangles where the anisotropy axes form 120° , these systems have a net magnetic moment and is paramagnetic. This agrees well with the low temperature $\chi_M T$ and $M(H)$ data, which are compatible with a non-vanishing magnetic moment in the ground state.

Figure 4. Relative orientation of the local magnetic moments for $\text{Dy}_3\cdot[\text{BPh}_4]$ (green arrows) with the closest coordinated oxygen atom also indicated in green colour (see Fig. S7 for the similar orientation of magnetic moments of $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$).

Because the Dy^{III} ions of the triangle in $\text{Dy}_3\cdot[\text{BPh}_4]$ and $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ have a high anisotropy and, as a result, a large energy gap between the ground and excited doublets (see Table 3), SMM with a high effective energy barrier U_{eff} is expected for these compounds. In agreement with the *ab initio* calculations, point charge crystal field calculations have shown that half-integer spins, like Dy^{III} ions, with trigonal prismatic geometries with or without apexes in the centre of the rectangular faces, are good candidates to show SMM behaviour.¹⁹

In order to study if these compounds exhibit slow relaxation of the magnetization and SMM behaviour, *ac* magnetic susceptibility measurements were performed as a function of the temperature and frequency under zero-static field for both $\text{Dy}_3\cdot[\text{BPh}_4]$ and $\text{Dy}_3\cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ with the aim of studying the dynamics of the magnetization (Figures 5-7 and Figures S9-S16). $\text{Dy}_3\cdot[\text{BPh}_4]$ displays a clear frequency dependence the out-of-phase (χ''_M) signals below ~ 15 K under zero *dc* field, typical of thermally activated relaxation process (Figure 5). The χ''_M vs. T plot shows a broad signal between ~ 4 K and 15 K in the range 100–1400 Hz but without reaching a neat maximum, which can be due to overlapping of different relaxation processes, including a faster quantum tunnelling relaxation. The latter process would be responsible of the increase of χ''_M below 4 K. However, in general this indicates that

Dy₃[BPh₄] exhibits slow relaxation of the magnetization and possibly SMM properties.

Figure 5. Temperature dependence of the out-of-phase χ''_{ac} signals under zero dc field (top) and 1 kOe (bottom) for **Dy₃[BPh₄]**. Solid lines are guides for the eye.

When the *ac* measurements were performed in the presence of a small external *dc* field of 1000 Oe to fully or partly suppress the quantum tunnelling relaxation of the magnetization (QTM), two peaks appear with maxima in the temperature ranges 9.79 K (1200 Hz)-5.0 K (40 Hz) and 4.4 K (1200 Hz)-3 K (40 Hz) for the slow (SR) and fast (FR) relaxation processes, respectively (Figure 5 bottom). It is worth mentioning that the observation of several thermally activated relaxation processes for crystallographically equivalent Dy^{III} ions is not unprecedented,²⁵ demonstrating the complexity of the relaxation processes occurring in the complexes containing 4f metal cations. Nevertheless, this phenomenon is more commonly observed for polynuclear Ln systems where the Ln^{III} occupy non-equivalent chemical environment.^{9f,26}

The Cole-Cole diagram for **Dy₃[BPh₄]** in the temperature range 10-6 K (Figure S12) for the *ac* susceptibility data obtained under a *dc* applied field of 1000 Oe, exhibits distorted semi-circular shapes and can be fitted using the generalized Debye model, affording α values (this parameter determines the width of the distribution of relaxation times, so that $\alpha = 1$ corresponds to an infinitely wide distribution of relaxation times, whereas $\alpha = 0$ represents a relaxation with a single time constant) in the range 0.51-0.6, which, as expected, suggest the existence of more than one relaxation process operating at low temperatures.

The temperature of the maxima in the χ''_{ac} vs. *T* plot and the corresponding frequencies were used in constructing the Arrhenius

plots for the SR and FR relaxation processes (Figure 6). The fit of

the data afforded an effective energy barrier for the reversal of the magnetization of 34.8(2) cm⁻¹ with $\tau_0 = 7.5 \times 10^{-7}$ s for the SR process and 19.5(2) cm⁻¹ with $\tau_0 = 3.75 \times 10^{-7}$ s for the FR process. The Arrhenius plot constructed with the relaxation times extracted from the fitting of the χ''_{ac} vs. frequency data to the Debye equation led to virtually identical values for the U_{eff} energy barrier.

Figure 6. Arrhenius plots of relaxation times for **Dy₃[BPh₄]** under 1 kOe. Black solid lines represent the best fitting of the experimental data to the Arrhenius equation.

Dynamic *ac* magnetic susceptibility measurements as a function of the temperature and frequency for **Dy₃·0.33[Dy(NO₃)₆]** (Figure 7) clearly show that, under zero *dc* field, this compound presents slow relaxation of the magnetization below ~ 15 K, with broad signals in the χ''_{ac} vs. *T* plot and a maximum at ~ 5 K for frequencies above 1200 Hz. The broadness of the signal suggests the existence of several relaxation processes. The fact that the χ''_{ac} components (Figure 7) do not go to zero below the maxima but increase below 3 K can be attributed to the presence of fast relaxation of the magnetization via a QTM mechanism through the thermal energy barrier between degenerate energy levels. The QTM relaxation process also affects the signals above 3 K, so that the thermal energy barrier could not be accurately extracted either from the maxima of the χ''_{ac} vs. *T* plot at different frequencies or from the fitting of the χ''_{ac} vs. frequency at different temperatures to the Debye model. In a 1000 Oe *dc* applied field, the *ac* susceptibility signals are three times more intense than under zero-field and the maxima move to higher temperatures in the χ''_{ac} vs. *T* plot (7.5 K at 1480 Hz). This behaviour suggests that quenching of the QTM fast relaxation process leads to slower relaxation of the magnetization. The χ''_{ac} signals do not go to zero even at *dc* fields as higher as 2500 Oe, which suggests either that the QTM is not fully suppressed by the field or the existence of an additional fast relaxation process with maxima below 2 K. Concerning the first suggestion, it should be noted that for non-integer spin systems, like Dy^{III}, transverse anisotropy do not facilitate QTM and this is mainly mediated by dipole-dipole interactions and/or hyperfine interactions.¹ In some instances, the sole application of a small *dc* field is not able to suppress the QTM process (as it occurs in our case), and a dilution process with an isostructural diamagnetic species is additionally needed. As for the second suggestion, the Dy^{III} ion belonging to the [Dy(NO₃)₆]³⁻ anion exhibits, as indicated elsewhere, an distorted icosahedral coordination polyhedron, which produces a quasi-spherical crystal field around the Dy^{III} ion that originates a very small splitting of the low-lying doublets states. This situation would lead to a very small thermal energy barrier and therefore the maxima in the χ''_{ac} vs. *T* plot could appear below 2 K.

Figure 7. Temperature dependence of the out-of-phase χ_M'' ac signals under zero dc field (top) and 1000 Oe (middle) for $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$. Solid lines are guides for the eye. Arrhenius plot for $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ under 1 kOe (bottom). Black solid lines represent the best fitting of the experimental data to the Arrhenius equation.

The fit of the semi-circular Cole-Cole plots of the $H_{dc} = 1000$ Oe data (Figure S16) in the temperature range 8.5–5 K to the Debye model afforded α values in the range 0.14–0.30, which, as for $\text{Dy}_3 \cdot [\text{BPh}_4]$, also suggest the existence of more than one relaxation process operating at low temperatures. The fit of the relaxation times vs. $1/T$ data in the 8.5–5 K temperature range to the Arrhenius law (see Figure 7) leads to a thermal energy barrier of $U_{\text{eff}} = 19.4(4) \text{ cm}^{-1}$ and $\tau_0 = 4.7 \times 10^{-6} \text{ s}$.

In order to discard cluster-glass behaviour in these complexes, we have analyzed the frequency-dependent shift of the maxima in the χ_M'' vs T curve using the Mydosh empirical parameter $\gamma = (\Delta T_f / T_f) / (\Delta \log f)$, where T_f is the temperature corresponding to the maximum in the χ_M'' vs T curve for each frequency (f) and ΔT_f is the difference between the highest and lowest blocking temperatures corresponding to the extremes of the frequency range under exploration.²⁷ The calculated shift parameters for the fast and slow

relaxation processes in $\text{Dy}_3 \cdot [\text{BPh}_4]$ of 0.35 and 0.28, respectively, are consistent with superparamagnetic behaviour (γ values > 0.1 are usually observed for this type of magnetic behaviour). In the case of $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$, $\gamma = 0.56$ and therefore the presence of glassiness can be also ruled out. The relative large γ value for $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ could be due to existence of a distribution of relaxation times. The absence of glassiness in $\text{Dy}_3 \cdot [\text{BPh}_4]$ and $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ together with the fact that the extracted τ_0 and U_{eff} values for these compounds are physically meaningful and similar to those previously reported for SMM systems support SMM behaviour for these compounds.

By Hall-based micromagnetometry, we extended the magnetic measurements down to lower temperatures. Figure 8 and figure S17 (between -5 T and 5 T) shows magnetic hysteresis loops for $T = 2.0$ and 0.4 K , respectively, sweeping the magnetic field at a constant rate of 150 Oe/s . For both compounds, a narrow though noticeable loop opens as the temperature decreases down to 0.4 K , evidencing the behavior of $\text{Dy}_3[\text{BPh}_4]$ and $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ as molecular magnets. We observe a remnant magnetization of 0.8 and $1.0 \text{ N}_\mu\text{B}$, and a coercive field of 120 and 130 Oe , for $\text{Dy}_3[\text{BPh}_4]$ and $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$, respectively (see insets of Fig. 8). The existence of quantum tunneling at zero-field would explain why the hysteresis observed at 0.4 K is rather small. For this temperature and sweep rate, the hysteresis loops of both compounds show a step-like magnetization occurring at ca. 1 T .

Figure 8. For $\text{Dy}_3[\text{BPh}_4]$ (top) and $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ (bottom), magnetic hysteresis loops, within $-2 < H/T < 2$, for $T = 0.4$ and 2.0 K , as collected by Hall micromagnetometry. Isothermal magnetization data collected for $T = 2.0 \text{ K}$ (empty markers), using a commercial SQUID magnetometer, are depicted for comparison. Insets: magnification near zero applied field for $T = 0.4 \text{ K}$.

The relatively large quantum tunneling and the need to add a static field to determine the dynamic properties can be also

anticipated by the relatively large calculated g_x and g_y components (see Table 3).²³ Since in both dysprosium compounds the magnetic exchange interaction between the Dy^{III} ions inside the Dy₃ triangle is very weak, the observed relaxation process should have a single-ion origin. If so, a question immediately arises: why for **Dy₃·[BPh₄]** and **Dy₃·0.33[Di(NO₃)₆]**, having Dy^{III} ions inside the Dy₃ triangle with very close DyO₈ geometry and similar values for the energy gap between the ground and the first excited state, the thermal energy barrier is twice bigger for the former? The answer could be found in the eventual existence of larger dipole-dipole interactions for **Dy₃·0.33[Di(NO₃)₆]** than for **Dy₃·[BPh₄]** whose effects, as indicated above, cannot be eliminated by application of an small magnetic field. The larger dipole-dipole interactions for **Dy₃·0.33[Di(NO₃)₆]** would favour the QTM process thus reducing U_{eff} in a larger extent than in **Dy₃·[BPh₄]**. Finally, the fact that the effective thermal energy barrier for **Dy₃·[BPh₄]** and **Dy₃·0.33[Di(NO₃)₆]** are much lower than the calculated energy gap between ground and first Kramers' doublets can be due, in addition to the existence of QTM promoted by the dipole-dipole interactions, to limitations inherent to the *ab initio* quantum calculations.

Conclusion

We have succeeded in obtaining two new examples of Dy₃ triangles **Dy₃·[BPh₄]** and **Dy₃·0.33[Di(NO₃)₆]**, as well as their Gd₃ analogues, in which Dy^{III} ions are connected by triple phenoxo-di- μ -3-methoxo bridges. *Ab initio* calculations show that Dy^{III} ions, with biaugmented trigonal prismatic geometry, exhibit high axial anisotropic ground Kramers' doublets and a large energy gap between the ground and first excited doublets. The orientation of the magnetic moments is mainly dominated by the accommodation of the *f* electron density of the Dy^{III} centers to reduce the electron repulsion with the ligands. Thus, for an almost spherical distribution of the same nature ligands, the direction of the shortest Dy-O bond distance controls the magnetic moment orientation. For the studied Dy₃ complexes, the shortest distance corresponds to an oxygen atom out of Dy₃ plane, thus, the local moments are almost perpendicular to such plane. Taking into account this fact and the weak antiferromagnetic coupling found for such complexes, there is no cancellation of the total moment for the Dy₃ complexes. Hence, as expected, both compounds exhibit SMM behaviour.

Experimental Section

General methods and materials: All syntheses were performed in ambient laboratory atmosphere. All reagents and solvents were purchased from Sigma-Aldrich and were used as received. Dy(NO₃)₃·6H₂O was synthesized by dissolving slight excess of Dy₂O₃ in hot 50 % (v/v) nitric acid. Undissolved oxide was removed by decantation and the solution was concentrated by heating. The Dy(NO₃)₃·6H₂O was precipitated from the solution during the cooling/in fridge. Ligand H₂L was synthesized according to literature.²⁸

Synthesis of [Dy₃(μ_3 -OCH₃)₂(μ -HL)₃(NO₃)₃][BPh₄·4CH₃OH·H₂O] (Dy₃·[BPh₄]**). 0.1 mmol (46 mg) of Dy(NO₃)₃·6H₂O and 0.1 mmol (43 mg) of H₂L were weighted in 20 ml sample vial. 10 ml of methanol was added and the reagents were dissolved by heating and stirring. 0.05 mmol (17 mg) of NaBPh₄ and 0.2 mmol (28 μ l) of triethylamine was added in 6 ml of methanol and the solution was stirred thoroughly. The clear solution was filtered through cotton plug and was left to crystallize at room temperature overnight. Well shaped colourless crystals formed, which were separated by filtration and washed with cold methanol. Yield: 66 mg (83 %). Elemental analysis: C₁₀₂H₁₄₃BDy₃N₉O₃₁ (H₂O and 4 CH₃OH) (2489.59): calcd. C 49.21, H 5.79, N 5.06; found C 49.23, H 5.34, N 5.40. The same reaction but using Gd(NO₃)₃·6H₂O instead of Dy(NO₃)₃·6H₂O afforded the **Gd₃·[BPh₄]** Yield: 65 mg (80 %). Elemental analysis: C_{99.83}H₁₃₈BGd₃N₉O_{29.79} (3 CH₃OH) (2423.48): calcd. C 49.48, H 5.74, N 5.20; found C 49.75, H 5.46, N 5.25.**

Synthesis of [Dy₃(μ_3 -OCH₃)₂(μ -HL)₃(NO₃)₃][Di(NO₃)₆]_{0.33}·CH₃OH·6H₂O (Dy₃·0.33[Di(NO₃)₆]**). 0.266 mmol (122 mg) of Dy(NO₃)₃·6H₂O and 0.2 mmol (86 mg)**

of H₂L were weighted in 20 ml sample vial. 12 ml of methanol were added and the reagents were dissolved by heating and stirring. 0.4 mmol (56 μ l) of triethylamine was added and the solution was stirred thoroughly. The clear solution was filtered through cotton plug and was left to crystallize at room temperature overnight after which it was placed in freezer for 2 days. Formed colourless crystals were separated by filtration and washed with cold methanol. Yield: 42 mg (25 %). Elemental analysis: C₇₅H₁₀₉BDy_{3.33}N₁₁O_{37.43} (6 H₂O and CH₃OH) (2304.73): calcd. C 39.09, H 4.77, N 6.69; found C 39.01, H 4.95, N 6.76. The same reaction but using Gd(NO₃)₃·6H₂O instead of Dy(NO₃)₃·6H₂O afforded the **Gd₃·0.33[Gd(NO₃)₆]** complex. Yield: 46 mg (30 %). Elemental analysis: C_{75.50}H_{118.94}BDy_{3.33}N_{11.01}O_{37.03} (~3.5 H₂O and 1.5 CH₃OH) (2297.80): calcd. C 39.09, H 4.77, N 6.69; found C 39.01, H 4.95, N 6.76.

X-Ray Crystallography: Crystallographic data for complexes **Dy₃·[BPh₄]**, **Dy₃·0.33[Di(NO₃)₆]** and **Gd₃·0.33[Gd(NO₃)₆]** were collected with a Nonius-Kappa diffractometer equipped with CCD area-detector using Mo-K α radiation (λ = 0.71073 Å). SADABS absorption correction was applied to the data for **Dy₃·[BPh₄]** and **Dy₃·0.33[Di(NO₃)₆]** and **Gd₃·0.33[Gd(NO₃)₆]**.²⁹ For **Gd₃·[BPh₄]**, the data collection was made with Agilent SuperNova dual wavelength diffractometer equipped with Atlas CCD area detector using Cu-K α radiation and CrysAlisPro program package.³⁰ The empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was performed using CrysAlisPro program. The structures were solved by direct methods using SIR97³¹ and SHELXS-97³² programs and full-matrix, least-squares refinements on F² were performed using the SHELXL-97³² or Olex2³³ programs. All figures were drawn with Diamond 3.³⁴ Selected crystallographic data is collected in Table S3.

All determined structures contain considerable amounts of disorder either in the complex units or in the solvents of crystallization. In both complexes **Dy₃·[BPh₄]** and **Gd₃·[BPh₄]** the aminoethylmorpholine sidearm of the ligand is disordered in two places which could be refined with approximate 63:31 and 54:46 occupancy ratios, respectively. Furthermore, one phenyl ring of the tetraphenyl borate anion is disordered in six different positions hence the occupation of the disordered carbons in the rings are fixed to 0.167. The unit cells also contain disordered methanol and/or water molecules as solvents of crystallization. Most of these molecules cannot be refined with full occupancies hence the unit cells contain non-integer number of atoms. In complex **Gd₃·0.33[Gd(NO₃)₆]** the disordered solvent molecules were treated with solvent mask option as implemented in the Olex2 program.³³ For all other complexes the solvent mask (or SQUEEZE as implemented in PLATON program package³⁵) did not produce any better result than the refinement of partially occupied solvent molecules. In addition, in **Dy₃·0.33[Di(NO₃)₆]** the thermal motion of the methyl group in one of the μ_3 -bridging methoxides is so large that the carbon atom of the group cannot be refined anisotropically.

CCDC-969288 (**Dy₃·[BPh₄]**), CCDC-969289 (**Dy₃·Di(NO₃)₆**), CCDC-969290 (**Gd₃·[BPh₄]**), CCDC-969291 (**Gd₃·Gd(NO₃)₆**) contain 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.

Magnetic Properties: The variable temperature (2-300 K) magnetic susceptibility measurements on polycrystalline samples of complexes **Dy₃·[BPh₄]**, **Gd₃·[BPh₄]**, **Dy₃·0.33[Di(NO₃)₆]** and **Gd₃·0.33[Di(NO₃)₆]** under an applied field of 1000 Oe were carried out with a Quantum Design SQUID MPMS XL-5 device. *Ac* susceptibility measurements under different applied static fields were performed using an oscillating *ac* field of 3.5 Oe and *ac* frequencies ranging from 1 to 1500 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 grainlike samples consisted of collections of small crystallites of ca. 10⁻³ mm³.

Computational studies: DFT calculations were performed using the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code³⁶ together with the PBE functional.³⁷ Only valence electrons are included in the calculations, with the core being replaced by norm-conserving scalar relativistic pseudopotentials factorized in the Kleinman-Bylander form.³⁸ The pseudopotentials are generated according to the procedure of Trouiller and Martins.³⁹ For gadolinium atoms, we used the pseudopotential and triple- ζ basis set proposed by Pollet *et al.*⁴⁰ In the calculations, values of 50 meV for the energy shift and 250 Ry for the mesh cutoff have been employed because they provide a good compromise between accuracy and computer time to estimate exchange coupling constants.

To calculate the exchange coupling constant (*J*) a high-spin state (the three gadolinium are parallel aligned, hence *S* = 21/2) and a low-spin solution (because the complexes have a C₃ symmetry) have been computed. For GGA functionals, such as the PBE expression used in our calculations, the broken-symmetry approximation without spin-projection has been employed⁴¹⁻⁴³ to calculate the *J* value through the following equation:

$$J = \frac{E_{LS} - E_{HS}}{2S\uparrow S\downarrow} \quad (3)$$

CASSCF+RASSI calculations were carried out employing the MOLCAS package,⁴⁴ this method is particularly suited for the study of the low-energy spectra of lanthanide complexes with unquenched angular momentum because it allows for a multideterminant description of the system's wavefunctions and incorporates the effect of spin-orbit coupling mixing. The procedure comprises two steps: (i) Calculation of the spin-orbit free wavefunctions by means of a standard CASSCF step and (ii) Inclusion of spin-orbit interaction between the previously converged solutions by the restricted active space state interaction method (RASSI). Spin Hamiltonian parameters (in this case g factors for the eight lower Kramers' doublets for the local Dy^{III} centers) are obtained using the SINGLE_ANISO routine and magnetic coupling between Dy^{III} ions is modeled through the POLY_ANISO program, as implemented in the MOLCAS 7.8 software package.⁴⁵ Technical details about the calculated models can be found from the Supporting Information.

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Single-molecule magnets

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Two C_3 symmetric Dy_3^{III} Complexes with Triple Di- μ - Methoxy- μ -Phenoxo Bridges, Magnetic Ground State and SMM behaviour

New Dy_3 triangles. Two series of C_3 symmetric Dy_3 and Gd_3 complexes with different counter anions have been prepared. *Ab initio* calculations show that Dy^{III} ions exhibit high axial anisotropic ground Kramers' doublets, the local magnetic moments being almost

perpendicular to the molecular plane thus leading to a paramagnetic ground state. The large energy gap between the ground and first excited doublets of the Dy^{III} ions promotes slow relaxation of the magnetization and in both complexes.

SUPPORTING INFORMATION

Two C_3 Symmetric Dy_3^{III} Complexes with Triple Di- μ -Methoxy- μ -Phenoxo Bridges, Magnetic Ground State and SMM Behaviour

Mikko M. Hänninen, Antonio José Mota, Daniel Aravena, Eliseo Ruiz, Reijo Sillanpää, Agustín Camón, Marco Evangelisti, Enrique Colacio

Figure S1. Distorted icosahedral coordination polyhedron for the $[\text{Dy}(\text{NO}_3)_6]^{3-}$ anion in $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$.

Table S1. Continuous Shape Measures Calculations for **Dy₃·[BPh₄]**

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

Structure [ML8]

OP-8	HPY-8	HBPY-8	CU-8	SAPR-8
TDD-8	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8
JSD-8	TT-8	ETBPY-8		
28.806,	20.691,	14.916,	11.891,	4.460,
4.044,	12.277,	26.641,	2.863,	1.588,
5.119,	12.345,	22.225		

Table S2. Continuous Shape Measures Calculations for the Dy^{III} ion inside the Dy₃ triangle in **Dy₃·0.33[Dy(NO₃)₆]**

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

Structure [ML8]

OP-8	HPY-8	HBPY-8	CU-8	SAPR-8
TDD-8	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8
JSD-8	TT-8	ETBPY-8		

28.933, 20.934, 15.047, 12.186, 4.406,
3.777, 13.322, 27.309, 2.803, 1.431,
5.422, 12.635, 22.535

Table S3. Selected crystallographic parameters for **Dy₃·[BPh₄]**, **Dy₃·0.33[Dy(NO₃)₆]**, **Gd₃·[BPh₄]** and **Gd₃·0.33[Gd(NO₃)₆]**.

Complex	Dy₃·[BPh₄]	Dy₃·0.33[Dy(NO₃)₆]	Gd₃·[BPh₄]	Gd₃·0.33[Gd(NO₃)₆]
Formula	C ₁₀₂ H ₁₄₃ BDy ₃ N ₉ O ₃₁	C ₇₅ H ₁₀₉ Dy _{3.33} N ₁₁ O _{37.43}	C _{99.83} H _{138.10} BGd ₃ N ₉ O _{29.79}	C ₁₄₈ H _{209.88} Gd _{6.67} N _{22.02} O _{64.06}
<i>M_r</i>	2489.56	2305.33	2423.42	4370.89
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal
Space group	<i>P</i> -3 (<i>147</i>)	<i>R</i> -3 (<i>148</i>)	<i>P</i> -3 (<i>147</i>)	<i>R</i> -3 (<i>148</i>)
<i>a</i> (Å)	17.3063(15)	17.1370(3)	17.3008(7)	17.1750(5)
<i>b</i> (Å)	17.3063(15)	17.1370(3)	17.3008(7)	17.1750(5)
<i>c</i> (Å)	21.8388(16)	62.2948(17)	21.88420(9)	62.388(3)
<i>α</i> (°)	90	90	90	90
<i>β</i> (°)	90	90	90	90
<i>γ</i> (°)	120	120	120	120
<i>V</i> (Å ³)	5664.6(8)	15843.5(6)	5661.8(4)	15937.7(10)
<i>Z</i>	2	6	2	3
<i>D_c</i> (g cm ⁻³)	1.46	1.45	1.43	1.37
<i>T</i> (<i>K</i>)	123	123	123	123
<i>μ</i> (MoK _α)(cm ⁻¹)	2.036	2.412	11.827 ^a	2.127
Obs. unique reflections	6663	6202	6725	7520
<i>R_{int}</i>	0.0822	0.0817	0.0307	0.1296
Parameters	481	401	426	385
<i>R_I</i> ^b	0.0821 (0.0568) ^c	0.0834 (0.0568)	0.1028 (0.0865)	0.1149 (0.0662)
<i>wR₂</i> ^d	0.1423 (0.1283)	0.1449 (0.1298)	0.2637 (0.2463)	0.1591 (0.1451)

^aCuK_α radiation ^b $R_I = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^cValues in parentheses for reflections with $I > 2\sigma(I)$.

^d $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$, where $P = (2F_o^2 + F_c^2)/3$.

Figure S2. The capped sticks/space fill presentation of the disordered anion/solvent filling the cup formed by $[\text{Dy}_3]^+$ cation in $\text{Dy}_3 \cdot [\text{BPh}_4]$ (left) and $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ (right).

Figure S3. Temperature dependence of the $\chi_M T$ product for $\text{Gd}_3 \cdot [\text{BPh}_4]$. The black solid line represents the best fit with the indicated Hamiltonian. Inset: Field dependence of the magnetization. The black and red solid line represent Brillouin function for three isolated Gd^{III} ions and the best fit with the $J = -0.16 \text{ cm}^{-1}$ and $g = 2.07$.

Figure S4. Temperature dependence of the $\chi_M T$ product for $\text{Gd}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$. The black solid line represents the best fit with the indicated Hamiltonian. Inset: Field dependence of the magnetization. The black and red solid line represent Brillouin function for three isolated Gd^{III} ions and the best fit with $J = -0.17 \text{ cm}^{-1}$ and $g = 2.02$.

CASSCF+RASSI calculations: The local magnetic properties of the Dy^{III} complexes were modeled by constructing truncated geometries from the full X-Ray structure. The coordination environment of the Dy^{III} ion of interest was preserved while the remaining Dy sites were replaced by *ab initio* model potentials (AIMP) of the diamagnetic La^{III} ion (Figure S5-S7). The active space in the CASSCF calculations comprised 9 electrons in 7 orbitals, with a 8s7p5d4f2g1h basis set for Dy, 3s2p1d for O and N, 3s2p for C and 2s for H, La^{III} ions were represented with the La.ECP.deGraaf.0s.0s.0e-La(LaMnO₃) *ab initio* model potential. Simultaneous fit of the magnetization and magnetic susceptibility curves was performed employing the POLY_ANISO routine with an equal weight for both datasets.

Figure S5.(top) Geometric model for $\text{Dy}_3 \cdot [\text{BPh}_4]$. Color code: orange (Dy), blue (La), red (O), black (C), white (H). (bottom) Geometric model for the Dy_3 triangle in $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$. Color code: orange (Dy), blue (La), red (O), black (C), white (H).

Figure S6. Geometric model for the $\text{Dy}(\text{NO}_3)_6$ in $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$. Color code: orange (Dy), red (O), light blue (N).

Figure S7. Relative orientation of the local magnetic moments for $\text{Dy}_3 \cdot 0.33[\text{Dy}(\text{NO}_3)_6]$ (green arrows) with the closest coordinated oxygen atom also indicated in green color.

Figure S8. (left) Partial Charges assigned to the charged ligands. The rest of the atoms have zero charge. (right) Anisotropy axes for the Dy^{III} ions (orange lines). The local magnetic moments form an angle with the Dy_3 plane of 71.5° , which is almost coincident with that extracted using CASSCF *ab initio* calculations.

Figure S9, Frequency dependence of the χ_M'' ac signals at zero dc field for $\text{Dy}_3 \cdot [\text{BPh}_4]$. Solid lines are guides for the eye.

Figure S10. Temperature dependence of the out-of-phase $\chi_M' ac$ signals under 1000 Oe dc field for **Dy₃•[BPh₄]**. Solid lines are guides for the eye.

Figure S11. Frequency dependence of the χ''_M component at different temperatures under an applied *dc* field of 1000 Oe for **Dy₃•[BPh₄]**. Solid lines represent the best fits to the Debye model.

Figure S12. Cole-Cole plot under an applied *dc* field of 1000 Oe for **Dy₃·[BPh₄]**. Solid lines represent the best fits to the Debye model.

Figure S13, Frequency dependence of the χ''_M *ac* signals at zero *dc* field for **Dy₃·0.33[Dy(NO₃)₆]**. Solid lines are guides for the eye.

Figure S14. Temperature dependence of the out-of-phase χ_M' *ac* signals under 1000 Oe for **Dy₃·0.33[Dy(NO₃)₆]**. Solid lines are guides for the eye.

Figure S15. Frequency dependence of the χ_M'' component at different temperatures under an applied *dc* field of 1000 Oe for **Dy₃·0.33[Dy(NO₃)₆]**. Solid lines represent the best fits to the Debye model.

Figure S16. Cole-Cole plot under an applied dc field of 1000 Oe for **Dy₃·0.33[Dy(NO₃)₆]** . Solid lines represent the best fits to the Debye model.

Figure S17. For $\text{Dy}_3[\text{BPh}_4]$ (top) and $\text{Dy}_3 0.33[\text{Dy}(\text{NO}_3)_6]$ (bottom), magnetic hysteresis loops, within $-5 < H/T < 5$, for $T = 0.4$ and 2.0 K, as collected by Hall micromagnetometry. Isothermal magnetization data collected for $T = 2.0$ K (empty markers), using a commercial SQUID magnetometer, are depicted for comparison. Insets: magnification near zero applied field for $T = 0.4$ K.