

Article



Engineering Mononuclear Ln(III) Complexes with a Pseudo-Macrocyclic Hexadentate N₄O₂ Schiff Base Ligand Exhibiting Slow Magnetic Relaxation [†]

Ismael Francisco Diaz-Ortega ^{1,2}, Yating Ye¹, Jesus Jover ³, Eliseo Ruiz ^{3,*}, Enrique Colacio ^{1,*} and Juan Manuel Herrera ^{1,*}

- ¹ Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada and Unidad de Excelencia en Química (UEQ), Avenida Fuentenueva s/n, 18071 Granada, Spain; ifdior@ual.es (I.F.D.-O.); yatingwsy@ugr.es (Y.Y.)
- ² Departamento de Química y Física-CIESOL, Universidad de Almería, Carretera Sacramento s/n, 04120 Almería, Spain
- ³ Departament de Química Inorgánica and Institut de Recerca de Química Teórica i Computacional, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain; jesus.jover@qi.ub.edu
- * Correspondence: eliseo.ruiz@qi.ub.edu (E.R.); ecolacio@ugr.es (E.C.); jmherrera@ugr.es (J.M.H.)
- ⁺ This article is a tribute to Professors Miguel Julve and Francesc Lloret on the occasion of their retirement (Miguel sadly passed away very recently). They can be considered two of the most active, outstanding, and brilliant researchers in the field of Molecular Magnetism based on Coordination Complexes have achieved key milestones in this field over the last forty-five years and, consequently, contributed decisively to its development. Both of them and their collaborators at the University of Valencia and beyond, by subtly playing with the tools offered by Coordination Chemistry, have deliberately designed and prepared new and interesting molecular materials with aesthetic structures and outstanding magnetic properties. In addition, Miguel and Paco are very nice and friendly people who always helped many of us to walk along the exciting and attractive road of Molecular Magnetism. Thank you very much for your friendship, support, and teachings.

Abstract: We report here the synthesis of a series of nine coordinated mononuclear Ln^{III} complexes $[LnL_1Cl_2(DMF)]Cl\cdot2.5DMF$ and $[LnL^1(L_2)_2]Cl\cdot4CH_3OH$ ($Ln^{III} = Gd^{III}$, Dy^{III} , Er^{III} and Yb^{III} , $HL_2 = 9$ -anthracenecarboxylic acid), where L1 is a hexadentate N_4O_2 Schiff base ligand prepared from the condensation of 1,10-phenanthroline-2,9-dicarbaldehyde and semicarbazone. The X-ray crystal structures of these complexes show the Ln^{III} ions to possess $LnN_4O_2Cl_2$ and LnN_4O_4 coordination spheres, which can be considered to be derived from a hexagonal bipyramidal geometry, with the ligand in the equatorial plane and the anions (chloride or 9-antracenecarboxylate) in axial positions, which undergo distortion after coordination of either a molecule of DMF or a bidentate coordination of the 9-anthracenecarboxylate ligand. All these compounds exhibit field-induced slow magnetization relaxation (SMR). The absence of SMR at zero field due to QTM, as well as the processes involved in the magnetic relaxation under a field of 0.1 T, have been justified on the basis of theoretical calculations and the distortion of the respective coordination spheres. The severe discrepancy between the calculated and experimental thermal energy barriers for the Dy^{III} complexes seems to indicate that the relaxation occurs with the contribution of spin–vibrational coupling, which is favored by the flexibility of the ligand.

Keywords: single-molecule magnets; lanthanides; molecular magnetism

1. Introduction

The field of molecular magnetism experienced a major boost with the discovery of single-molecule magnets (SMMs) [1–10]. These nanoscale molecule-based magnets are paramagnetic metal complexes exhibiting both quantum (quantum tunneling of the magnetization (QTM), quantum coherence, and quantum oscillations) and classical (slow relaxation of the magnetization, leading to magnetic hysteresis and remnant magnetization at zero field below the commonly named blocking temperature, T_B) properties. Owing to



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). this intriguing association of physical properties, SMMs possess great potential for creating a new generation of ultrahigh-density data storage, spin-qubits for quantum computing, and spintronic devices [1–11]. The SMM behavior is tied to the existence of a large magnetic moment, a bistable ground state (a classical binary memory requires two degenerate states between which magnetization can be switched), and magnetic anisotropy. The latter issue is of paramount importance for observing SMM behavior, because the blocking of the magnetization below T_B is due to an energy barrier that mainly depends on the magnetic anisotropy, which in turn arises from the combined action of spin–orbit coupling and crystal field effects [1–10]. In view of this, it is not surprising that the use of Ln^{III} ions to construct SMMs allowed this area of research to enter into a fascinating and fruitful new stage of development.

Numerous examples of SMMs containing Dy^{III}, Tb^{III}, Er^{III}, Ho^{III} and even Nd^{III}, Tm^{III} and Yb^{III} lanthanide ions have been reported so far [1–18]. Among these systems, those of mononuclear nature, also named Mononuclear SMMs (MSMMs) or Single-Ion Magnets (SIMs), are the best choice for achieving high-performance SMMs. This is because in these mononuclear complexes, the magnetic anisotropy, which depends on the crystal field (CF), can be deliberately modulated by playing with the coordination environment around the lanthanide metal ion, which ultimately depends on the electronic and steric effects of the ligands. In connection with this, experimental and theoretical studies carried out on Ln^{III}-based SIMs have shown that for oblate ions (Dy^{III}, Tb^{III}, Ho^{III} and Nd^{III}), their axial anisotropy is maximized when the crystal field is axial (repulsive contacts are minimized), which can be reached with weak equatorial and strong axial CF components. For prolate lanthanide metal ions such as Er^{III}, Nd^{III} and Yb^{III}, weak axial and strong equatorial CF components are required to generate the anisotropic energy barrier [19–23]. In spite of that, it is of paramount importance to engineer molecular vibrations to control the spin lifetime of SMM complexes [24]. The best SMM properties have been observed for Dy^{III}-based SIMs because of the large magnetic anisotropy and Kramers nature of the Dy^{III} ion. In this case, the strong axial anisotropy stabilizes the largest $M_{\rm I} = \pm 15/2$ ground state and leads to a larger separation from the excited states [1–23]. Thus, dysprosium sandwich metallocenes with large axial (easy-axis) anisotropy and negligible rhombicity exhibit T_B and U_{eff} values as high as 1540 cm⁻¹ and 80 K, respectively [25–27]. Nevertheless, the record is held by the mixed-valence Ln^{III} - Ln^{II} dinuclear metallocene complex $[Dy_2I_3(CpiPr_5)_2]$ with $U_{eff} = 2347$ K and $T_B = 80$ K. In this compound, the collinearity of the anisotropy axes and the strong 4f-radical Ising exchange interaction result in a large separation of the first and excited states and the suppression of QTM [28].

Taking into consideration that the ultimate goal in this field of research is the incorporation of high-efficiency SMMs in devices for technological applications, these systems must be stable at ambient conditions, and this is not the case for Ln^{III}-based metallocenes. In view of this, thermal-, air- and humidity-stable monometallic complexes with axial symmetry, such as pentagonal and hexagonal bipyramids, have been designed with oblate Ln^{III} ions, some of which present insignificant transverse anisotropy, suppressed QTM and high-performance SMM behavior [29–34]. A good strategy for achieving this kind of system is using macrocyclic ligands containing weak donor atoms coordinated in the equatorial positions, whereas donor atoms with high electronic density are strongly bonded in axial positions. The magneto-structural properties of axial mononuclear SMMs containing macrocyclic ligands at the waist have recently been reported, demonstrating the efficacy of the proposed approach [35,36]. Moreover, complexes containing macrocyclic ligands generally show great stability at ambient conditions. Pseudo-macrocyclic polydentate ligands would also be a good choice for constructing axial SIMs stable at ambient conditions. In fact, some examples of Dy^{III}-based PBPY-7 SMMs have been reported so far [37–41]. However, to the best of our knowledge, there are no reported examples of HBPY-8 SMMs containing hexacoordinate pseudomacrocycles as ligands.

In this paper, we have focused on the challenge of synthesizing a new series of Ln^{III}-based SMMs showing pseudo-HBPY-8 geometry, using the hexadentate pseudo-

macrocyclic ligand 2,2'-((1,10-phenanthroline-2,9-diyl)bis(methanylylidene)]-bis(hydrazin-1-carboxamide) (L_1 in Scheme 1), which presents a high tendency to bond the Ln^{III} centers around their equatorial coordination positions. This ligand has been previously used to prepare Eu^{III}, Lu^{III} and Y^{III} derivatives [42], some of which show interesting properties as anion sensors.

The crystal structures showed that ligand L_1 encapsulated the Ln^{III} ions in their cleft with additional solvent molecules and/or counterions occupying the axial coordination positions. Firstly, we prepared a series of complexes of the formula $[LnL_1Cl_2(DMF)]Cl\cdot2.5DMF$, [Ln = Yb(1a), Er(2a), Dy(3a), Gd(4a)], which are isostructural to the complex $[Tb(L_1)Cl_2(DMF)]Cl$ previously reported by Albrecht et al. [11]. Additionally, we prepared a second series of complexes of the formula $[LnL_1(L_2)_2]Cl\cdot4CH_3OH$, [Ln = Yb(1b), Er(2b), Dy(3b), Gd(4b)], where the axially coordinated chloride anions and DMF molecules were replaced by the strongly coordinating ligand 9-anthracene carboxylate in order to generate an axially stressed ligand field around the Ln^{III} centers (Scheme 1). Here, we report the X-ray structures, dc and ac magnetic properties, ab initio calculations and luminescence properties of these two series of compounds. The aim of this work is not only to prepare a new series of potential Ln^{III} -SMMs but also to study how this ligand replacement affects the magnetic properties.

2. Experimental

2.1. Materials and General Methods

All chemical reactants and solvents were obtained from commercial sources (Merck, Burlington, MA, USA) and used as received. Ligand L_1 was prepared as described previously by Albrecht et al. [42].

Synthesis of the Complexes

[LnL₁Cl₂(DMF)]Cl·2.5DMF, [Ln = Yb(1a), Er(2a), Dy(3a), Gd(4a)]: To a suspension of L₁ (0.2 mmol) in 10 mL of methanol, one molar equivalent of the corresponding Ln(III) chloride salt dissolved in a minimal amount of the same solvent was added. The resulting solution was gently heated for 10 min and then dried under a vacuum, resulting in the precipitation of an orange solid. The slow diffusion of diethyl ether into a DMF solution of these precipitates gave a good yield of single crystals of complexes 1a-4a.

Yb(1a): Yield: 64%; elemental anal. for C_{26.5}H_{38.5}Cl₃N_{11.5}YbO_{5.5}: C, 35.94; N, 18.19; H, 4.38; found: C, 36.51; N, 18.00; H, 4.14.

Er(2a): Yield: 67%; elemental anal. for $C_{26.5}H_{38.5}Cl_3N_{11.5}ErO_{5.5}:$ C, 36.18; N, 18.31; H, 4.41; found: C, 36.40; N, 18.74; H, 4.51.

Dy(3a): Yield: 65%; elemental anal. for C_{26.5}H_{38.5} Cl₃N_{11.5}DyO_{5.5}: C, 36.37; N, 18.41; H, 4.43; found: C, 36.79; N, 18.27; H, 4.72.

Gd(4a): Yield: 69%; elemental anal. for C_{26.5}H_{38.5}Cl₃N_{11.5}GdO_{5.5}: C, 36.59; N, 18.52; H, 4.46; found: C, 37.29; N, 18.34; H, 4.56.

[LnL₁(L₂)₂]Cl·4CH₃OH, [Ln = Yb(1b), Er(2b), Dy(3b), Gd(4b)]: To a suspension of L₁ (0.2 mmol) in 10 mL of methanol, one molar equivalent of the corresponding Ln(III) chloride salt dissolved in a minimal amount of the same solvent was added. To the resulting solution, two equivalents of 9-anthracenecarboxylic acid (L₂, 0.4 mmol) and triethylamine (0.4 mmol) dissolved in 5 mL of methanol were added dropwise with stirring. The resulting orange solution was reduced in volume to about 5 mL and then diethyl ether was allowed to diffuse. Well-formed single crystals of complexes 1b–4b appeared after 48–72 h.

Yb(1b): Yield: 80%; elemental anal. for C₅₀H₄₇ClN₈YbO₁₀: C, 53.21; N, 9.93; H, 4.20; found: C, 53.36; N, 10.30; H, 4.00.

Er(2b): Yield: 81%; elemental anal. for C₅₀H₄₇ClN₈ErO₁₀: C, 53.49; N, 9.98; H, 4.22; found: C, 53.68; N, 10.35; H, 3.98.

Dy(3b): Yield: 82%; elemental anal. for C₅₀H₄₇ClN₈DyO₁₀: C, 53.72; N, 10.02; H, 4.24; found: C, 53.30; N, 10.38; H, 4.63.

Gd(4b): Yield: 81%; elemental anal. for C₅₀H₄₇ClN₈GdO₁₀: C, 53.94; N, 10.07; H, 4.26; found: C, 54.26; N, 10.47; H, 3.94.

2.2. Physical Measurements

Elemental analyses were carried out at the Centro de Instrumentación Científica of the University of Granada with a Fisons-Carlo Erba EA 1108 Elemental Analyser. Direct (dc) and alternating (ac) current susceptibility measurements in different applied statics fields were performed with an oscillating ac field of 3.5 Oe and ac frequencies ranging from 50 to 1400 Hz with a Quantum Design SQUID MPMS XL-5 device. Ac magnetic susceptibility measurements in the range of 1000–10,000 Hz were carried out with a Quantum Design Physical Property Measurement System in an oscillating ac field of 5 Oe.

2.3. Computational Methodology

Low-energy spectra and g factors of the eight lowest Kramer's doublets were obtained by means of Complete Active Space Self-Consistent Field and Restricted Active Space State Interaction (CASSCF + RASSI) calculations, as implemented in the open MOL-CAS 18.09 software package [43]. The method is divided into two steps: (1) CASSCF calculations for three different multiplicities (sextet, quartet and doublet); (2) the effect of spin–orbit coupling on the basis of the converged wavefunctions obtained in the previous step is included by the RASSI method. Spin Hamiltonian parameters (such as g factors) can be calculated from the wavefunctions resulting from the state interaction step employing the SINGLE ANISO program [44] implemented in the open MOLCAS 18.09 package. We included 21, 128 and 98 roots for the sextet, quartet and doublet Dy^{III} CASSCF calculations, 35 quartets and 112 doublet states were included for the Er^{III} systems, and 7 doublet states were used for the Yb^{III} calculations. The employed basis set has the following contractions: Dy[9s8p6d4f3g2h], Er[9s8p6d4f3g2h], Yb[9s8p6d4f3g2h], O[4s3p2d1f], N[4s3p2d1f], Cl[5s4p2d1f], C[3s2p], H[2s]. The structure of the model was extracted from the corresponding X-ray structure without any ligand truncation.

2.4. Single-Crystal Structure Determination

Suitable crystals of complexes **1a–4a** and **1b–4b** were mounted on a Bruker D8 Venture (Mo K α radiation, $\lambda = 0.71073$ Å, Photon 100 CMOS detector). Details of the crystals, data collection and refinement parameters are shown in Tables S1 and S2. Once the data were processed (raw integration, merging of equivalent reflections and empirical correction of the absorption), the structures were solved by either Patterson or direct methods and refined by full-matrix least-squares on weighted F² values using the SHELX–2014 suite of programs [45] integrated in Olex2 [46]. Selected bond angles and distances can be found in Tables S3–S5. For structures **1b–3b**, several solvent molecules in the asymmetric unit were found to be disordered over multiple positions and could therefore not be modeled satisfactorily. They were removed from the electron density map using the OLEX solvent MASK command. These structures crystallize in the non-centrosymmetric *Cc* space group. The calculated Flack parameters reflect the presence of racemic twinning. CCDC numbers 2392736–2392743 contain the supplementary crystallographic data for this article. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

3. Results and Discussion

3.1. Syntheses and Crystal Structures

The synthetic procedures for the preparation of complexes **1a–4a** and **1b–4b** are shown in Scheme 1. For complexes **1a–4a**, the reaction of L1 with the corresponding LnCl3 salt in methanol afforded in all cases microcrystalline orange solids soluble in dimethylformamide (DMF). When diethyl ether was slowly diffused into concentrated DMF solutions of such solids, the complexes appeared as single crystals in good yields. With respect to complexes 1b–4b, single crystals of these complexes were obtained by slow diffusion of diethyl ether into a methanolic solution containing L1, 9-anthracenecarboxylic acid (L2), triethylamine and the corresponding LnIII chloride salt in a 1:2:2:1 molar ratio.



Scheme 1. Synthesis of complexes 1a-4a and 1b-4b.

X-ray studies revealed that complexes 1a-4a are isostructural to the Tb^{III} analog complex described previously by Albrecht et al. [42]. The complexes crystallize in the triclinic crystallographic system, the *P*-1 space group. The lanthanide ions exhibit an n = 9coordination number, with the hexadentate L₁ ligand enveloping the Ln^{III} centers, creating an equatorial $Ln(N_4O_2)$ fragment (Figure 1a). $Ln-N_{L1}$ bond distances are slightly longer than those of Ln–O_{L1} (see Table S5). Within the Ln–O_{L1} bond distances, Ln–O1 (ranging between 2.527 Å for 1a and 2.551 Å for 4a) is significantly longer than Ln–O2 [2.342 Å (1a)–2.391 Å (4a)]. Bond distances decrease as the ionic radii of the Ln^{III} centers decrease due to lanthanide contraction. L1 is slightly twisted with a deviation from planarity that decreases as the Ln^{III} ionic radius raises. To illustrate this writhing, we have considered a plane containing atoms Ln1, N4 and N5 (Figure S1a). O1 (above the plane) and O2 (below) are separated from this plane by a distance ranging between 1.194 Å (1a) and 1.185 Å (1b) and between 0.573 Å (1a) and 0.488 Å (4a), respectively. The coordination around the Ln^{III} centers is completed by two chloride counterions (Cl1 and Cl2) axially coordinated at opposite sides of L_1 and one oxygen atom (O3) that belongs to a molecule of DMF. According to the continuous-shape-measures method (CShMs) [47,48], the coordination sphere geometry around the Yb^{III} center in 1a is close to ideal C_s (muffin) and C_{2v} (hulahoop) geometries (CShMs values of 3.773 and 3.787, respectively). As the ionic radius of the Ln^{III} center increases in the rest of the series (2a–4a), the coordination geometries around the Ln^{III} centers progressively deviate from a muffin-like (Cs) polyhedron and approach a hula-hoop coordination environment (Table S6). In all the cases, several DMF molecules of crystallization and a third chloride counterion, which ensures electroneutrality, are present in the structures.



Figure 1. X-ray structures of complexes **1a** (**a**) and **1b** (**b**). Hydrogen atoms, crystallization solvent molecules and non-coordinated counterions have been omitted for the sake of clarity. Ellipsoids are drawn at 50% probability.

Complexes **1b–4b** are isostructural and crystallize in the monoclinic *Cc* space group. The main structural motif in this set of complexes is not very different from that observed for **1a–4a**. The ligand L_1 also embraces the Ln^{III} centers describing a wristed equatorial plane (see Figure 1b). In these cases, however, the axial coordination positions around the Ln centers are occupied by two L_2 ligands via their carboxylate groups. On one side of the LnL_1 platform, the carboxylate group acts as a bidentate ligand (O2 and O3 atoms), while that on the opposite side is monodentate (O5). The Ln^{III} centers exhibit a LnO_5N_4 coordination sphere with a geometry intermediate between ideal hula-hoop (C_{2v}) and spherically relaxed capped cube (C_{4v}) polyhedra (see Table S6). As the ionic radius of the Ln^{III} ion decreases, the C_{2v}-CShMs parameter increases, and the geometry becomes closer to C4v. For the LnL1 unit, Ln-NL1 bond distances are, as expected, longer than those of Ln- O_{L1} (see Table S5). As in the previous series, the twist of the ligand L_1 can be illustrated by considering the distances between atoms O1 and O2 and the mean plane defined by atoms N4–Ln1–N5 (Figure S1b). These distances range between 1.041 Å (1b) and 1.003 Å (3b) and between 0.787 Å (1b) and 0.745 Å (4b) for O1 and O2, respectively. Compared to Ln–Cl bond distances in **1a–4a**, axial Ln–O_{L2} bond distances are significantly shorter (see Table S5). In particular, the Ln–O5 bond distances (corresponding to the monodentate carboxylate group) are significantly shorter than those of Ln–O3 and Ln–O4 (which correspond to the bidentate carboxylate group). In general, all bond distances increase slightly as the size of the Ln^{III} center increases due to lanthanide contraction. Several methanol and water crystallization molecules exist in the structure connected between them and with the $[LnL_1(L_2)_2]$ entity through hydrogen bonds.

3.2. Magnetic Properties

The thermal variations of the $\chi_M T$ product (χ_M is the magnetic susceptibility measured under an applied *dc* magnetic field of 0.1 T) in the temperature range 2 K–300 K for complexes **1a–4a** and **1b–4b** are presented in Figure S2 and the numerical data are listed in Table 1. At room temperature, the $\chi_M T$ values are close to those expected for magnetically isolated Ln^{III} ions under the free-ion approximation. For Gd^{III} derivatives **4a** and **4b**, the $\chi_M T$ products remain almost constant throughout the range of temperatures studied, as expected for such an isotropic ion with negligible intermolecular magnetic exchange interactions and zero-field splitting (ZFS). Conversely, for complexes **1a–3a** and **1b–3b**, the $\chi_M T$ product gradually decreases as the temperature falls to 2 K, which is due to the thermal depopulation of the excited m_J sublevels arising from the ligand field splitting of the LS ground terms ${}^2F_{7/2}$, ${}^4I_{15/2}$ and ${}^6H_{15/2}$ of the Yb^{III} (**1a** and **1b**), Er^{III} (**2a** and **2b**) and Dy^{III} (**3a** and **3b**) ions, respectively.

Table 1. DC magnetic data for the complexes studied in this work.

Complex	Ln ^{III} Ground State	Theoretical $\chi_M T$ [cm ³ K mol ⁻¹] ^[a]	Experimental $\chi_M T_{300 \text{ K}}/\chi_M T_{2\text{K}}$ [cm ³ K mol ⁻¹]	Theoretical $M_{ m sat} \ [{ m N}\mu_B]^{[{ m b}]}$	Experimental $M_{sat} [N\mu_B]$ (T = 2K, H = 5 T)	CASSCF $\chi_M T$ 300 K/2 K [cm ³ K mol ⁻¹]	CASSCF $M_{\text{sat}} [N\mu_B]$ (T = 2 K, H = 5 T)
1a 1b	Yb ^{III} , ${}^{2}F_{7/2}$, $g_{J} = 8/7$	2.57	2.39/1.11 2.44/1.38	4	1.65 1.94	2.49/1.85 2.43/1.65	1.92 1.86
2a 2b	$Er^{III}, {}^{4}I_{15/2}, g_{J} = 6/5$	11.48	11.45/5.44 11.8/6.98	9	4.02 5.4	11.26/7.95 11.18/6.73	4.43 4.22
3a 3b	$Dy^{III}, {}^{6}H_{15/2}, g_J = 4/3$	14.17	14.35/10.92 14.42/10.60	10	5.56 5.73	13.93/11.86 13.83/12.27	5.06 5.02
4a 4b	$Gd^{III}, {}^{8}S_{7/2},$ $g_{J} = 2$	7	7.55/7.36 7.65/7.39	7	7.23 7.41		

^[a] $\chi_M T = \frac{N\beta^2}{3K} \left\{ g_J^2 J(J+1) \right\}; {}^{[b]} M = Ng J\mu_B; J = L+S; g_J = \frac{3}{2} + \frac{S_T(S_T+1) - L(L+1)}{2J(J+1)}.$

The *M* vs. H plots at T = 2 K (Figure S2b,d) for all the complexes studied in this work show a relatively sharp increase in the magnetization at fields below 1.5 T. At higher fields, the increase in the magnetization is smoother, almost reaching saturation at H = 5 T. For the Gd^{III} derivatives (**4a** and **4b**), the saturation value is very close to that expected for an isotropic S = 7/2 system. For the rest of the complexes, the M_{sat} values are lower than those calculated (Table 1), which can be mainly attributed to crystal field effects giving rise to significant magnetic anisotropy [49,50].

The M_{sat} values for the Dy^{III} complexes (**3a** and **3b**), as well as the value of $\chi_M T$ product where all the temperature- and frequency-dependent curves converge, which is close to that expected for an isolated $M_{\text{J}} = \pm 15/2$ ground state (12.5 cm³ mol⁻¹ K), indicate the axial nature of the ground state (Figure S3). In the case of compound **3a**, the $\chi_M T$ value (13.9 cm³ mol⁻¹ K) is higher than expected, which can be due to a slight orientation of the microcrystals in the magnetic field.

3.3. Dynamic Magnetic Properties

In order to determine if the Yb^{III}, Er^{III} and Dy^{III} complexes presented in this work exhibit slow magnetic relaxation properties, ac dynamic susceptibility measurements were taken as a function of temperature and frequency. Initially, the measurements were carried out in the absence of an external dc magnetic field. Under these conditions, none of the complexes exhibited SMM behavior, probably due to the fast relaxation of the magnetization through quantum tunneling (QTM). When a dc external field of 0.1 T was applied (this was the field leading in all cases to the larger relaxation time at 4 K; see Figures S5–S8), frequency- and temperature-dependent out-of-phase signals appeared, thus indicating the existence of slow magnetic relaxation in these compounds. For the Yb^{III} derivatives 1a and **1b**, the χ_M vs. *T* plots (Figure 2, right) show the frequency dependence of χ_M with maxima between 4.0 K (1000 Hz) and 5.7 K (10,000 Hz) and between 2.4 K (1000 Hz) and 3.9 K (10,000 Hz), respectively. At low temperatures, the χ_M " signals do not clearly tend to zero, which could be indicative that the QTM has not been fully canceled. The Cole-Cole plots (Figure 2, right) in the range 2.0 K–5.0 K displayed semicircular shapes with α values between 0.27 (2.0 K) and 0.038 (5.0 K) and between 0.106 (2.0 K) and 0.201 (5.0 K) for 1a and **1b**, respectively. Considering that α values close to zero indicate a single relaxation process, whereas $\alpha = 1$ corresponds to an infinitely wide distribution of relaxation times, the α values observed for both complexes at low temperatures suggested the existence of several competitive relaxation processes. The temperature dependence of the relaxation times was extracted from the fitting of the frequency dependence of χ_{M} " to the Debye model (Figure S8). The τ^{-1} vs. *T* is generally described by the following equation:

$$\tau^{-1} = AT + \tau_{\text{OTM}}^{-1} + BT^n + \tau_0 \exp^{\left(-\frac{U\text{eff}}{k_{\text{B}}T}\right)}$$
(1)

where the two first terms represent the direct and QTM relaxation processes, respectively, whereas the third and fourth terms describe Raman and Orbach relaxation processes. Taking into consideration that the magnetic relaxation in Yb^{III} complexes generally takes place through a Raman process [17,51–53], the extracted τ vs. *T* data were fitted to a combination of Raman and QTM (second and third terms in Equation (1)). An excellent fit was obtained with magnetic parameters B, n and τ_{QTM}^{-1} given in Table 2. Although the magnetic relaxation does not take place through a thermally activated Orbach process, for comparative purposes, we have phenomenologically extracted the energy barriers (U_{eff}) for the reversal of the magnetization and the relaxation times (τ_0) from the fit of the high-temperature τ vs. *T* data to an Arrhenius plot (Table 2).



Figure 2. Yb^{III} complexes **1a** (**top**) and **1b** (**bottom**): thermal dependence of the out-of-phase χ_M " signal under a 1000 Oe dc field (**left**). Arrhenius plots of the relaxation time under a 1000 Oe dc field (**middle**; red and green lines represent the best fit of the experimental data to the Arrhenius equation and to the Raman + QTM relaxation processes, respectively). Cole–Cole plots under H_{dc} = 1000 Oe (**right**).

Compound	Orbach (H _{dc} = 0.1 T) ^[a]		Orbach/Raman/QTM				
	$U_{\rm eff}$ [K]	$ au_0$ [s]	B ($s^{-1} K^{-n}$)	п	$ au_{ m QTM} [m s]$	$U_{\rm eff}$ [K]	$ au_0 [\mathrm{s}]$
1a	37.3	$2.3 imes 10^{-8}$	0.18 ^[d]	7.3 ^[d]	$5.9 imes 10^{-4} [d]$		
1b	20.3	$7.9 imes10^{-8}$	41.6 ^[d]	5.4 ^[d]	$3.8 imes 10^{-4} [d]$		
2a	39.4	$2.8 imes10^{-9}$	0.02 ^[e]	9	$2.3 imes10^{-4}$ [e]	43.3 ^[e]	$2.2 imes 10^{-9} \text{[e]}$
2b	21.1	$1.3 imes10^{-7}$	0.03 ^[e]	9	$3.2 imes 10^{-3}$ [e]	16.8 ^[e]	$7.9 imes 10^{-7}{ m [e]}$
3a	≈ 8.9 ^[b]	pprox3.3 $ imes$ 10 ^{-6 [b]}	≈0.002 ^[c]	≈2.5 ^[c]			
3b	≈5.3 ^[b]	$pprox 8.5 imes 10^{-6} {\rm [b]}$	≈0.001 ^[c]	≈1.7 ^[c]			

Table 2. U_{eff} and τ_0 values for the reported complexes studied in this work.

^[a] Calculated from the high-temperature data of the Arrhenius plot. ^[b] Using Equation (3). ^[c] Using Equation (4). ^[d] Using a combination of Raman and QTM in Equation (1). ^[e] Using a combination of Orbach, Raman and QTM in Equation (1).

The magnetic parameters extracted from this fit indicate that the replacement of the axial chloride and DMF ligands by the carboxylate groups of the anthracene carboxylate ligand gives rise to a moderate acceleration of the magnetization relaxation.

The Er^{III} complexes 2a and 2b also exhibited field-induced SMM behavior with neat frequency-dependent χ_M " maxima that appeared between 3.1 K (1000 Hz) and 4.6 K (10,000 Hz) and between 2.5 K (1,000 Hz) and 4.4 K (10, Hz) for complexes 2a and 2b, respectively (Figure 3, left). $U_{\rm eff}$ and τ_0 were extracted for both complexes by fitting the calculated relaxation times τ at different temperatures to an Arrhenius law and are listed in Table 2. The deviation of the data from linearity observed at low temperatures (Figure 3, middle) suggests the existence of several competitive relaxation processes. In agreement with this, the Cole-Cole plots in the range 3.0 K–5.0 K display semicircular shapes with α values between 0.14 (3.0 K) and 0.04 (5.0 K) and between 0.104 (2.0 K) and 0.04 (5.0 K) for 2a and 2b, respectively (Figure 3, right). As in the case of the Yb^{III} complexes, the χ_M " signals do not clearly tend to zero below the maxima, which suggests that the QTM has not been fully suppressed by the field. The best fit was obtained by considering that only Orbach, Raman and QTM processes (fourth, second and third terms in Equation (1), respectively) contribute simultaneously to magnetic relaxation. In order to avoid overparametrization, the n parameter for the Raman process was fixed to the expected value for a Kramers ion (n = 9) [54]. A very good fit was obtained with the parameters given in Table 2. Compared to the simple Arrhenius law, as usual, higher U_{eff} and lower τ_0 values were obtained from the fit of the experimental data to this equation. Here, again, the magnetization relaxation

is slightly accelerated when the DMF molecule and the chloride counterions axially coordinated to the Er^{III} centers are replaced by anthracene carboxylate groups (Table 2). It is worth noting that a good-quality fit can also be obtained for **2a** and **2b** when Equation (1) is used (see Table 2). However, bad-quality fits were obtained in both cases by using a combination of Raman and Orbach processes.



Figure 3. Er^{III} complexes **2a** and **2b**: thermal dependence of the out-of-phase χ_M ["] signal under a 1000 Oe dc field (**Left**). Arrhenius plots of the relaxation time under a 1000 Oe dc field (**middle**; red and green lines represent the best fit of the experimental data to the Arrhenius equation and to the Orbach + QTM relaxation processes, respectively). Cole–Cole plots under H_{dc} = 1000 Oe (**right**).

Regarding the Dy^{III} derivatives, complex **3a** also exhibits field-induced slow relaxation of the magnetization, but without maxima at temperatures above 2 K. Complex **3b** presents maxima in the χ_M signals only at frequencies higher than 6000 Hz (Figure 4). In view of this, we can affirm that either the energy barrier for the reversal of the magnetization is too small to be blocked at temperatures above 2 K or that fast QTM relaxation exists.



Figure 4. Dy^{III} complexes **3a** and **3b**: thermal dependence of the out-of-phase χ_M signal under a 1000 Oe dc field (**Left**). Plots of $\ln(\chi_M''/\chi_M')$ vs. T^{-1} (**middle**; solid lines represent the best fit to Equation (3)). Plots of $\ln(\chi_M''/\chi_M')$ vs. $\ln T$ (**right**; solid lines represent the best fit to Equation (4)).

The ac data for **3a** and **3b** could not be fitted satisfactorily, neither by a Debye model nor by a generalized Debye model including a distribution of relaxation times, because the relaxation rates were too close to or beyond the experimental limit of our equipment of 10 kHz. To overcome this problem, and to make a quantitative comparison with the Yb^{III} and Er^{III} derivatives, we have used an alternative approach to obtain the relaxation parameters from the ac data, which is based on the fact that the ratio between the out-of-phase and in-phase ac susceptibility can be expressed in an approximate manner as (Equation (2)) [55],

$$\chi_M'/\chi_M'' = 2\pi f \tau \tag{2}$$

where f is the frequency of the ac magnetic field.

The substitution in this equation of the relaxation time (τ) by its expression for each relaxation mechanism (Orbach or Raman) allows us to determine the respective relaxation parameters. If we assume that, hypothetically, the relaxation occurs entirely through an Orbach relaxation mechanism, for which $\tau = \tau_0 \cdot \exp(U_{\text{eff}}/k_{\text{B}}T)$, after applying natural logarithms, the equation becomes as follows:

$$\ln\left(\frac{\chi_M''}{\chi_M'}\right) = \ln\left(2\pi f\tau_0\right) - \frac{U_{\rm eff}}{k_{\rm B}T} \tag{3}$$

The effective energy barrier U_{eff} and τ_0 could be approximately estimated by fitting the experimental χ''/χ' data in the high-frequency region to this equation (Figure 4). Indeed, the extracted U_{eff} and τ_0 values for these complexes (Table 2) are significantly smaller than those calculated for the Yb^{III} and Er^{III} derivatives. Nevertheless, the U_{eff} values should be taken as phenomenological and may not represent the actual relaxation processes. In the presence of a magnetic field, direct/Raman processes should dominate in the studied low-temperature range. Bearing this in mind, we have also fitted the χ''/χ' data to the following equation:

$$\ln\left(\frac{\chi_M''}{\chi_M'}\right) = \ln\left(2\pi f C\right) - n(\ln T) \tag{4}$$

which was obtained by replacing τ in Equation (2) with its expression for Raman/direct processes ($\tau = CT^{-n}$). The data in the 3 K–5 K range for **3a** and those in the range 2.5–4 K for **3b** were fitted to Equation (4) using frequencies in the ranges 50–1,400 Hz and 1000–10,000 Hz, respectively, leading to the parameters $C \approx 1.6 \times 10^{-3}$ s and $n \approx 2.5$ for **3a** and $C \approx 0.0007$ and $n \approx 1.70$ for **3b** (Figure 4).

In both cases, the inverse of the relaxation times follows a temperature dependence close to T^2 , which could be ascribed to a resonance phonon trapping (RPT) mechanism. This process occurs when there are phonon-bottleneck effects, so that the energy of the lattice modes generated by the relaxing spins cannot be liberated fast enough into a thermal reservoir. These phonons can be reabsorbed by other spins, and the effective relaxation time becomes longer.

3.4. Ab Initio Calculations

In order to rationalize the experimental magnetization relaxation and to estimate the values of the thermal energy barrier for complexes **1a–3a** and **1b–3b**, we performed ab initio CASSCF (Complete-Active Space Self-Consistent Field)/RASSI + SO/SINGLE-ANISO calculations on their X-ray structures using open MOLCAS 18.09 [43]. The energy for the first four KDs and their g values for all the compounds are given in Table S7, whereas the g tensors for the ground KD and the energy of the first excited KD for these complexes (Δ) are given in Table 3. The calculated orientation of the main anisotropy axis and the ab initio computed blocking barrier for the magnetization reversal are given in Figures 5 and 6, respectively. The computed crystal field parameters are gathered in Table S8, whereas the calculated susceptibility and magnetization data derived from the ab initio calculations are given in Tables S9 and S10.

Table 3. Computed first excitation energies after including the spin–orbit effects (Δ) and *g* values for the ground-state Kramers' doublet of complexes **1a**/**1b**–**3a**/**3b**.

Complex	Δ (cm $^{-1}$)	gxx, gyy, gzz
1a	216.8	0.07, 0.12, 7.68
1b	257.9	0.52, 1.10, 7.16
2a	54.6	0.43, 0.71, 15.81
2b	64.1	0.74, 1.34, 14.52
3a	118.3	0.17, 0.36, 19.42
3b	241.7	0.03, 0.04, 19.81



Figure 5. CASSCF computed orientation of the main magnetization axis (g_{zz}) along the beta-spin density for the Yb^{III} complexes (**top**), Er^{III} complexes (**middle**) and Dy^{III} complexes (**bottom**).



Figure 6. Ab initio blocking barrier for the Yb^{III} complexes (**top**), Er^{III} complexes (**middle**) and Dy^{III} complexes (**bottom**). The blue, red and green arrows represent spin-phonon relaxation mechanisms and their transition magnetic moment matrix elements.

With regard to the Yb^{III} complexes, the main anisotropic axis for **1a** is almost included to the DyN_4O_2 mean plane and practically perpendicular with the pseudo-C₆ axis, whereas for **1b**, the main anisotropy axis is located within the plane (Figure 5, top). In **1a**, the shortest distances Yb–O2 and Yb–O3 are close to the mean plane of the pentadentate ligand, and therefore, the prolate electronic density is directed toward the axial positions perpendicular

to the DyN_4O_2 mean plane (close to the Yb–Cl bonds), thus reducing electronic repulsions. However, in the case of **1b**, the shortest Yb–O distances are by far those in axial or close to axial positions, and therefore, the electronic density of the Yb^{III} ion spreads out on the ligand plane, placing the main anisotropic axis in the plane and oriented along the bisectrix of the N6-Yb-O2 angle. The CASSCF-computed beta-spin density presents the prolate-like shape expected for a pure $M_I = \pm 7/2$ ground state with an almost spherical density with some holes in the region of the Yb-Cl bonds (for 1a) due to the unique 4f empty orbital. The $U_{\rm eff}$ values calculated through the first excited state of 216.8 and 257.9 cm⁻¹ are significantly larger than the experimental ones (extracted from the ac susceptibility measurements in the presence of a small magnetic field of 0.1 T, see Table 2). The calculated transition magnetic moments between the ground-state KD are close to zero with values of 0.04 and 0.27, respectively (Figure 6, top), indicating a weak QTM relaxation mechanism. Therefore, an efficient spin-relaxation mechanism without QTM has been predicted in Yb^{III} complexes, in agreement with our experimental observation [17,51–53]. These results suggest that spin relaxation occurs through phonon-activate processes, with the Raman, direct mechanisms or local-mode spin-relaxation being predominant, as generally observed for reported Yb^{III} field-induced mononuclear SMMs [53,56].

The ab initio calculations carried out on the Er^{III} complexes 2a and 2b show that the main anisotropic axis (Figure 5, middle) is close to be included in the mean plane of the hexadentate N_4O_2 ligand similar to those of the Yb(III) systems. This orientation is adopted to reduce the crystal field repulsion on the prolate electron density distribution of the Er^{III} ion with the short distances with the axial ligands. In this case, the mismatching between the orientation of the main magnetic axis and the axial direction of the coordination geometry can lead to a strong transverse magnetic anisotropy and fast magnetic relaxation at zero field [57]. In accordance with this hypothesis, the computed blocking barrier through the first excited state for **2a** and **2b**, respectively, is smaller than that for the Dy^{III} counterparts. Moreover, the computed transition magnetic moments for these compounds between the ground KD of 0.19 and 0.35, respectively (Figure 6, middle), point out the existence of QTM and fast magnetic relaxation. This behavior is in agreement with the absence of slow relaxation in **2a** and **2b**. After quenching the QTM by applying a small *dc* static magnetic field, the experimental $U_{\rm eff}$ values extracted for 2a and 2b are only slightly lower than those calculated, which may be due to limitations inherent to the method, spin-vibronic coupling and fast direct processes.

These complexes **3a** and **3b** show a highly anisotropic ground state ($M_I = \pm 15/2$) with strong axiality (g_{zz} ~20 and g_{xx} and $g_{\mu\nu}$ ~0). This is in agreement with the fact that for lower-symmetry complexes, like **3a** and **3b**, the ground KD state is mostly axial with $M_I = \pm 15/2$, whereas the orientation of the anisotropy axis depends on the symmetry and CF strength of the Dy^{III} coordination sphere. Nevertheless, this ground state is not of pure Ising type as the g_{xx} and g_{yy} tensor components are small but significant. The CASSCF-computed beta-spin density does not present the characteristic disk-like shape expected for a pure $M_I = \pm 15/2$ ground state, which points out that the ground state is instead mixed with other excited states. The spin density for **3a** and **3b** spreads out along the DyN₄O₂ coordination plane, and thus, the anisotropy axis is oriented perpendicular to this plane (Figure 5, bottom). It is worth noting that this orientation of the anisotropy axis in **3a** and **3b** is perpendicular to that observed for complexes with analogous hydrazone pentadentate ligands and PBPY-7 geometry [37–41]. This difference could be due to the fact that in the latter, the pentadentate ligand is deprotonated, leading to Dy-O distances in the equatorial plane that are significantly shorter than those found for **3a** and **3b**, where the ligand is found in a non-deprotonated form. In order to reduce the repulsion between the large CF in the equatorial plane of these PBPY-7 complexes with deprotonated hydrazone pentadentate ligands and the oblate electron density distribution of the Dy^{III} ground state, the anisotropic axis is located near the DyN_3O_2 plane. Additionally, the distortion of the Dy^{III} coordination sphere in **3a** and **3b**, where oxygen donor atoms with short Dy–O distances belonging to the hexadentate ligand and to the DMF molecule are located above

and below the DyN_4O_2 plane, could increase the contribution to the axial crystal field with respect to the situation where these donor atoms are much closer to this plane, as observed in hydrazone-based PBPY-7 complexes. For **3a** and **3b**, the orientation of the main magnetic axis matches well with the Dy–Cl direction in **3a** and with the Dy–O5 direction in **3b**, which are close to the axial direction of the coordination geometry, thus favoring the uniaxial anisotropy. The ab initio computed blocking barriers for the magnetization reversal for 3a and 3b are given in Figure 6 (bottom). The computed transverse magnetic moments for these compounds between the ground KD of 0.09 and 0.01 are near the threshold value of 0.1 generally assumed for efficient magnetic relaxation. Nevertheless, the accepted value for complete suppression of the QTM is $<10^{-6}$ [39]. Therefore, a non-negligible contribution of QTM is expected for these compounds, which would explain why 3a and 3b do not show slow magnetic relaxation at zero field. The computed transverse magnetic moments for the thermally assisted quantum tunneling of magnetization (TA-QTM) through the first excited state of 1.20 and 0.51 for complexes 3a and 3b, respectively, are larger than those connecting the ground KD, which suggest that, in the presence of a magnetic field, magnetic relaxation should take place predominantly through the first excited KD doublet with U_{calc} values of 118.3 and 241.7 cm⁻¹ for **3a** and **3b**, respectively. The larger U_{calc} value for **3b** could be due to the fact that the Dy-O5 bond distance, involving the oxygen donor atom of the monodentate carboxylate ligand in the axial position, is comparatively short (2.224 Å), thus favoring a stronger thermal energy barrier for **3b**. The large difference between the calculated and experimental thermal energy barrier could be due to dipolar intermolecular interactions that induce QTM, hyperfine interactions and spin-vibrational coupling [1–10,24], which were not considered in the ab initio calculations. Even in the presence of a small dc field, the slow relaxation is quite weak (the out-of-phase signal steadily increases when the temperature decreases), thus indicating that the QTM is not fully suppressed and/or the spin lifetime is severely restricted due to the coupling between the low-energy vibrational modes (the most populated at the low experimental temperatures) and the spin, thus inducing spin-relaxation at low temperatures through anharmonic Orbach and/or Raman mechanisms [29]. The flexible first coordination sphere could be responsible for low-energy vibration that provokes magnetization relaxation in the reported field-induced mononuclear SMMs [58,59].

Finally, we have also computed crystal field parameters (Table S8) to analyze the QTM between the ground-state KDs. The corresponding crystal field Hamiltonian is given as $H_{CF} = B_k^q O_k^q$, where B_k^q is the crystal field parameter while O_k^q is the Steven's operator. Larger non-axial B_k^q (where $q \neq 0$, and k = 2, 4, 6) terms than the axial B_k^q (where q = 0, and k = 2, 4, 6) terms are found to favor the QTM process. For all the reported complexes, both the axial and non-axial terms are found to be equal in strength, suggesting non-negligible relaxation via ground KDs, which agrees with the experimental results.

4. Conclusions

The above results allow us to extract the following conclusions: (i) The N₄O₂ hexadentate pseudo-macrocyclic Schiff base ligand (L1), prepared from phenanthroline dialdehyde and semicarbazide, does not form the expected mononuclear Ln^{III} complexes (Ln^{III} = Gd^{III}, Dy^{III}, Er^{III} and Yb^{III}) with hexagonal bipyramidal geometry (HBPY-8), where the ligand L1 would occupy the equatorial positions and two monodentate anions (either chloride or 9-anthracenecarboxylato) the axial positions. Instead, nine coordinated complexes were formed by the additional coordination of either a DMF molecule or the oxygen atom of a bidentate 9-anthracenecarboxylato anion, thus distorting the coordination sphere from the HBPY-8 geometry. (ii) None of the nine coordinated Ln^{III} complexes exhibit slow relaxations at zero field due to QTM, which has been supported by ab initio calculations. The QTM results from the transverse anisotropy were generated by the distortion of the coordination sphere and, in the case of the Er^{III} complexes, also by the mismatching of the main magnetic axis, which is located close to the mean plane of the coordinated pseudo-macrocyclic ligand, and the pseudoaxial direction of the coordination geometry. (iii) After the partial suppression of the QTM, by application of a small optimal dc field, all the complexes exhibit slow relaxation of the magnetization, which takes place through a combination of Raman and QTM for the Yb^{III} complexes, through a combination of Orbach, Raman and QTM for the Er^{III} complexes, and through a resonance-trapping mechanism for the Dy^{III} counterparts. (iv) The fact that the thermal energy barriers (U_{eff}) theoretically calculated for the Dy^{III} complexes are moderately high (118.3 and 241.7 cm⁻¹), whereas those extracted from experimental data are much smaller (a few cm⁻¹), seems to indicate that other relaxation processes, such the coupling between spin and vibrational molecular modes arising from the flexibility of the first coordination sphere, could govern the magnetization relaxation in these field-induced mononuclear SMMs.

In view of the above considerations and with the aim of disposing of very efficient Dy^{III}-based HBPY-8 SMMs with the ligand L1, we have planned to use bulky neutral (tri alkyl/aryl phosphine oxides) or anionic monodentate ligands (aromatic alkoxides, trialkyl or triaryl alkoxides, or silanoxides), with high electronic density on the oxygen donor atom, which after coordination in axial positions prevent steric hindrance in the coordination of additional ligands to the HBPY-8 coordination sphere.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/magnetochemistry10120104/s1, Figure S1: Molecular Representation, Figures S2–S8 Magnetic Measurements; Tables S1–S2: Crystallographic Data, Tables S3–S5: Bond Distances, Table S6: Continuous Shape Measures, Tables S7–S10 CASSCF results.

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