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Abstract: The complex [Dy(**L**)(tta)$_3$] with **L** the chiral 3-(2-pyridyl)-4-aza[6]-helicene ligand (tta$^-$ = 2-theonyltrifluoroaacetonate) has been synthesized in its racemic form and structurally and magnetically characterized. [Dy(**L**)(tta)$_3$] behaves as a single molecule magnet in its crystalline phase with the opening of an hysteresis loop at 0.50 K. These magnetic properties were rationalized by *ab initio* calculations.

Keywords: Single molecule magnets; Lanthanide; Helicene; Magnetic anisotropy; ab initio calculations

1. Introduction

The design of single molecule magnet (SMM), with the aim of enhance their peculiar magnetic properties, is a prolific field in the scientific community since decades.[1-3] Indeed SMMs can pave the way towards a new generation of materials as, for example, molecular qubits for quantum computing [4], memory storage devices [5] or spin valves [6]. In this framework, lanthanide ions are commonly exploited in the effort of reaching slower relaxation rates for the reversal of the magnetization. Indeed lanthanide are well classified by looking at their electron density distribution, ranging from oblate (planar) to prolate (axial) distribution.[7] This is due mainly to their strong spin-orbit coupling, that leads to ground states with large angular momentum *J* and to strong magnetic anisotropy. The crystal field, induced by the donor atoms of the ligands, acts only as a perturbation on the electron density distribution, leading to a fine-tuning of the electronic properties and so of the molecular magnetism. As a consequence, the careful choice of the lanthanide ion and of the ligands (and the symmetry) can be used to engineer novel SMMs. However still a complete elucidation of these magneto-structural correlations for these complexes is missing, even if progresses have been done in the past decades.[8-11]

For all the applications mentioned above, it is crucial to study the correlation between the SMM behavior and other physical properties as luminescence or redox activity.[12] The versatility of ligand chemistry can be exploited in this sense to achieve this coupling and may offer the possibility to have in a single compound, for instance, a magnetic emitting nanodevice.[13-15] Indeed, lanthanides have been intensively studied for their peculiar luminescence that covers a broad range of frequency (from visible to NIR) with line-shape emission bands and long lifetime of the excited states.[16-22] However they show very low absorption coefficients, since the f-f transitions are indeed prohibited (Laporte rule.[23] This results in ineffective direct excitation processes, especially in dilute solution. To tackle this problem indirect sensitization, using for example MLCT (Metal-Ligand charge transfer) transitions, has been developed by the mean of functionalization of ligands with organic chromophores acting as antennae.[24] In case the antenna is chiral, the solid-state properties might change between the enantiopure and the racemic crystals. On the other side, the magnetic properties

of these atoms can be used to modify the light adsorption in chiral compounds, an effect known as magneto-chiral dichroism.[25-26]

A first example of the coupling between a Dy^{III}-based SMM and a chiral antenna has been reported recently with the complex [Dy(**L**)(hfac)$_3$] with **L** = 3-(2-pyridyl)-4-aza[6]-helicene and hfac = 1,1,1,5,5,5-hexafluoroacetylacetone.[27] On the one hand the Dy^{III} ion, with its $^6H_{15/2}$ ground state, easily leads to Ising type of magnetic anisotropy in determined coordination spheres like N_2O_6 and this is achieve with the common bidentate 2,2′-bipyridine (bpy) ligand and three hfac ligands.[13,28-30] On the other hand, a 2,2′-bipyridine (bpy) ligand has been functionalized with a [6]-helicene to enhance the luminescence. Indeed, the latter presents a π-conjugated backbone of aromatic rings, configurationally stable for n ≥ 5, and their peculiar topology results in intense emission properties.[31-32] Moreover, [n]-helicene ligands are helically-shaped, so they possess an axial chirality despite the absence of enantiocenter. For all this properties, this family of ligands is widely employed for various applications, ranging from organic molecular electronics,[33] probes for detection of chirality and sensing devices [34] to molecular junction.[35]

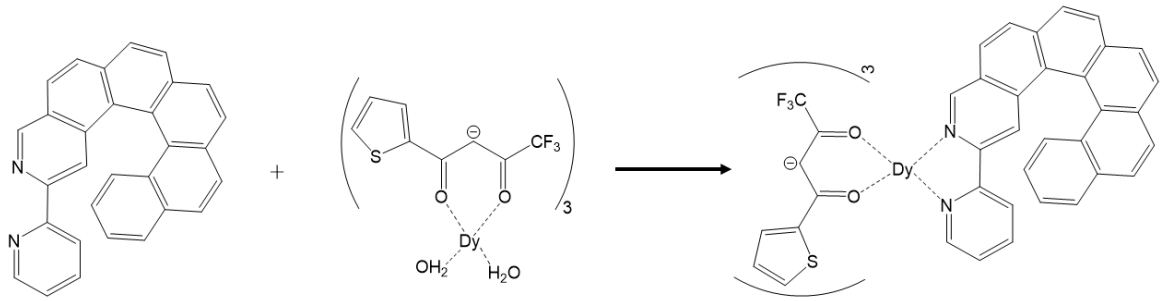
In the case of the [Dy(**L**)(hfac)$_3$] SMM,[27] the chirality of the ligand results in two possible crystal structures (racemic and enantiopure) with similar molecular arrangement but different packings. Interestingly, racemic and enantiopure crystals show notable different magnetic behavior, with the opening of a magnetic hysteresis only in the case of the enantiopure. Moreover, the calculated different nature (anti- and ferromagnetic) of the dipolar couplings between first-neighbors allows explaining the magnetic measurements (e.g. temperature dependence of $\chi_M T$).

With the aim to enhance the magnetic properties in this series of compounds, we present herein a novel derivative in which the hfac$^-$ ligand has been replaced by tta$^-$ (2-theonyltrifluoroaacetonate) ligands. Indeed it is well known in the literature [36-38] that the swapping of these two ligands leads to better magnetic properties. Therefore we report the synthesis, the single crystal X-ray structural analysis and the magnetic characterization along with extensive *ab initio* calculations of the novel compound, [Dy(**L**)(tta)$_3$] (**1**).

2. Results and Discussion

2.1 Structure

Complex **1** was obtained by the coordination reaction of the chiral 3-(2-pyridyl)-4-aza[6]-helicene [39] ligand (**L**) and tris(2-theonyltrifluoroaacetonate)bis(aqueous)Dy^{III} in CH_2Cl_2 (Scheme 1).



(**L**) $Dy(tta)_3{\cdot}2H_2O$ (**1**)

Scheme 1. Synthetic route to obtain **1**.

1 crystallizes in the triclinic centrosymmetric space group P-1 (Figures 1 and S1, Table S1). The Dy^{III} ion is surrounded by two nitrogen atoms and six oxygen atoms coming from the three 2-theonyltrifluoroaacetonate (tta$^-$) anions and the **L** ligand. The N_2O_6 coordination polyhedron can be described as a distorted square antiprism environment (D_{4d} symmetry, for SHAPE, Table S2).[40] Thus the replacement of the 1,1,1,5,5,5-hexafluoroacetylacetonate anions with tta$^-$ one confers an

higher symmetry for the coordination environment.[27] As already noted, such observation was already done for another complex stemming from group and it has a significant positive impact on the magnetic properties.[37-38]

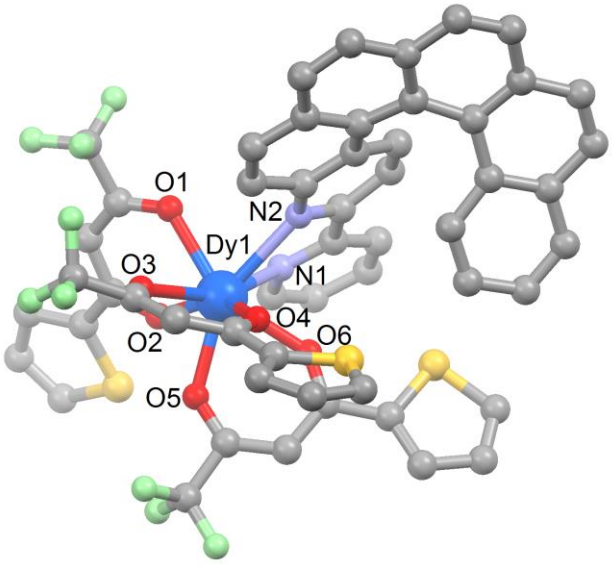


Figure 1. (a) Molecular structure of **1**. Hydrogen atoms and molecules of crystallization are omitted for clarity. Selected bond lengths: Dy1-N1, 2.560(3) Å; Dy1-N2, 2.549(3) Å; Dy1-O1, 2.341(3) Å; Dy1-O2, 2.296(3) Å; Dy1-O3, 2.359(3) Å; Dy1-O4, 2.356(3) Å; Dy1-O5, 2.322(3) Å; Dy1-O6, 2.341(3) Å.

Starting from the racemic mixture of **L**, both enantiomers are present in the cell. The crystal packing reveals that heterochiral dimers are formed with the presence of π-π interactions between the 2,2′-bipyridyl moieties (Figure 2) while an organic network runs along the *a* axis thank to π-π interactions between the helicenic parts. The Dy-Dy shortest intermolecular distance was measured equal to 8.935 Å which is similar to the distance measured in the complex involving the $Dy(hfac)_3$ metallo-precursor.

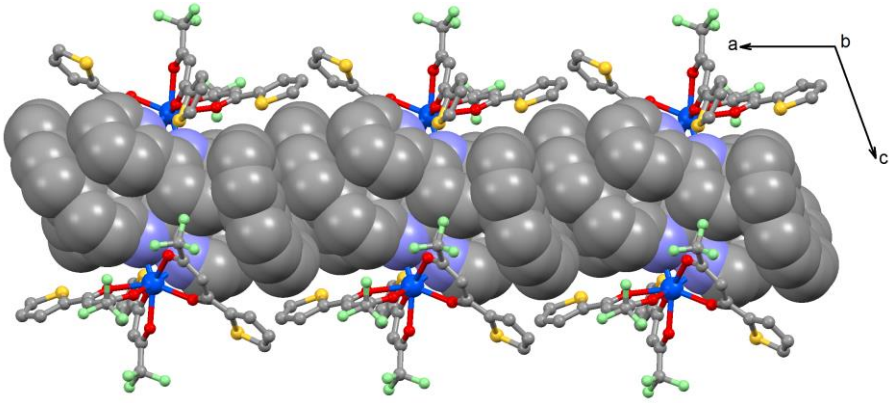


Figure 2. Crystal packing of **1** along the *a* axis. "Spacefill" and "ball and sticks" representations are used for **L** ligands and organometallic moieties, respectively.

2.2 Magnetic properties

2.2.1 Static magnetic measurements

The temperature dependence of $\chi_M T$ for the sample **1** is represented in Figure 3. The room temperature value is 13.96 $cm^3 \cdot K \cdot mol^{-1}$ in good agreement with the expected value of 14.17 $cm^3 \cdot K \cdot mol^{-1}$ for an isolated Dy^{III} ion.[41] On cooling, $\chi_M T$ decreases monotonically down to 11.20 $cm^3 \cdot K \cdot mol^{-1}$ due to the thermal depopulation of the M_J states. Below 5K, the more rapid decrease could be attributed to the presence of weak dipolar antiferromagnetic interactions as determined by quantum calculations on the analogue complex involving $hfac^-$ ancillary ligands.[27] The field dependence of the magnetization measured at 2.0 K reaches the value of 5.12 μ_B under a magnetic field of 50 kOe, which is far from the expected saturated value (Inset of Figure 3).

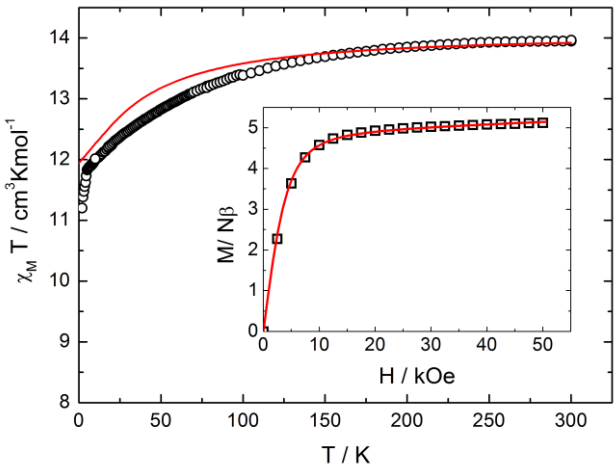


Figure 3. Temperature dependence of $\chi_M T$ for **1** (black circles). In inset the field variations of the magnetization at 2 K. Full red lines correspond to the simulated curve from ab initio calculations.

2.2.2 Dynamic magnetic measurements

The out-of-phase component of the ac susceptibility (χ_M'') of **1** was measured using immobilized crunched single crystals. It shows frequency dependence in zero external dc field but with clear maxima of the χ_M'' vs. ν curve (ν the frequency of the ac oscillating field) (Figure 4a). The frequency dependence of the ac susceptibility can be analyzed in the framework of the extended Debye model.[42-43] The temperature dependence of the relaxation time at zero field is extracted between 2.0 and 15.0 K (Table S3). The relaxation time follows the Arrhenius law $\tau = \tau_0 \exp(\Delta/kT)$ only above 12 K with $\tau_0 = 7.3(2) \times 10^{-7}$ s and $\Delta = 35.4(2)$ cm^{-1} (Figure 4d, open squares) while a thermally independent regime (meanly quantum tunneling of the magnetization, QTM) is observed at lower temperatures.

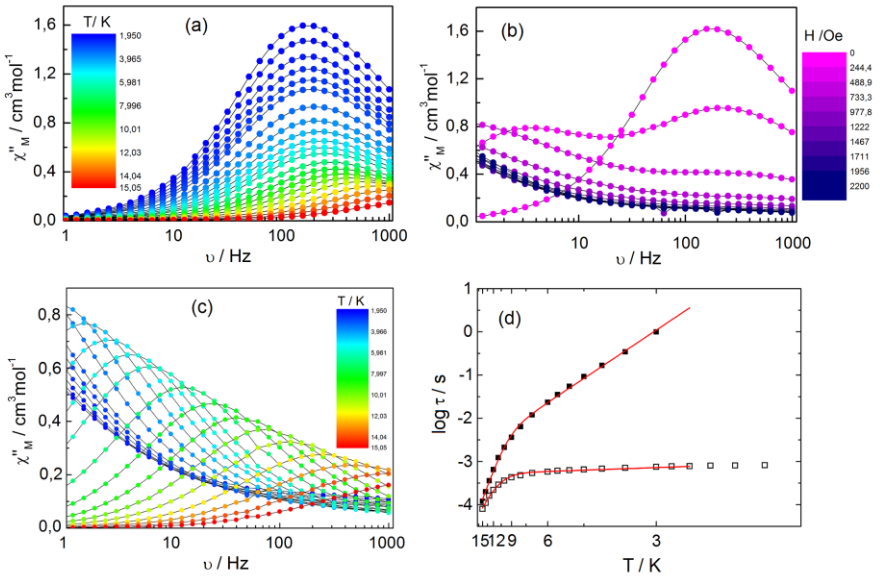


Figure 4. (a) Frequency dependence of χ_M'' between 2 and 15 K, (b) Scan field of the frequency dependence of χ_M'' at 2 K, (c) Frequency dependence of χ_M'' between 2 and 15 K under an applied magnetic field of 1000 Oe; (d) Temperature variation of the relaxation time measured in zero field (open squares) and in an external field of 1000 Oe (full squares) with the best fitted curve (red lines) in the temperature range of 2-15 K.

In order to reduce the QTM operating in this system, the optimal magnetic field of 1000 Oe was determined by a scan field (Figure 4b). The application of this moderate external dc field induces a slowing down of the magnetic relaxation with a shift of the maxima of the χ_M'' vs. ν curve at lower frequencies (Figure 4c) Once again the thermal dependence of the relaxation time of the magnetization can be fitted considering a thermally dependent regime above 10 K (Orbach process) ($\tau_0 = 2.0(7)\times10^{-7}$ s and $\Delta = 47.3(3)$ cm^{-1}) while at lower temperature the deviation from the linearity can be attributed to the operating two-phonon Raman process ($\tau = C\times T^n$ with $C = 4.8(6)\times10^{-3}$ and $n = 6.26(7)$).

Relaxation times on the order of few seconds is enough slow to observe the opening of the hysteresis loop at 0.50 K (Figure 5).

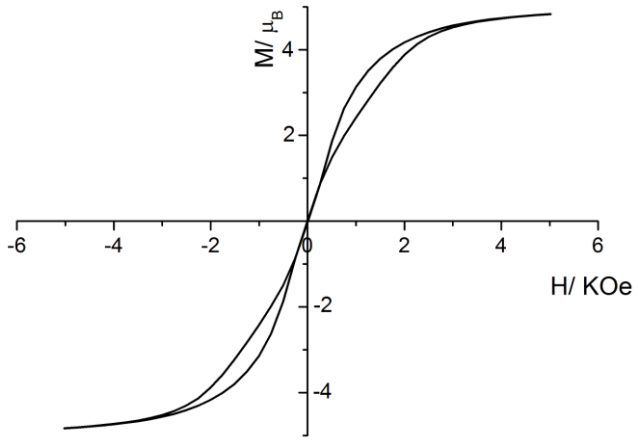


Figure 5. Magnetic hysteresis loop of **1** measured at 0.5 K.

2.2.3 Ab initio calculations

SA-CASSCF/RASSI-SO calculations were performed for **1** to rationalize the observed magnetic properties (see computational details). The calculated $\chi_M T$ *vs* T and M *vs* H (Figure 3) curves fairly

well reproduce the experimental curves. Calculations confirm the axial character of the magnetic anisotropy tensor of the ground Kramers doublet with large g_z values of 19.55 and almost negligible g_x and g_y values. The g_z value for Dy^{III} is close to the expected $g_z = 20$ for a pure $M_J = \pm |15/2\rangle$ ground state. This is confirmed by the calculated composition of $M_J = 0.94 |\pm15/2\rangle + 0.06 |\pm11/2\rangle$ for the ground doublet state of **1** (see Table S5 for the wavefunction composition). The calculated ground-state easy axis (Figure 6) for the Dy^{III} ion is oriented perpendicular to the plane formed by the 2,2′-bipyridine moieties as expected for an oblate ion in this coordination sphere.[31][36]

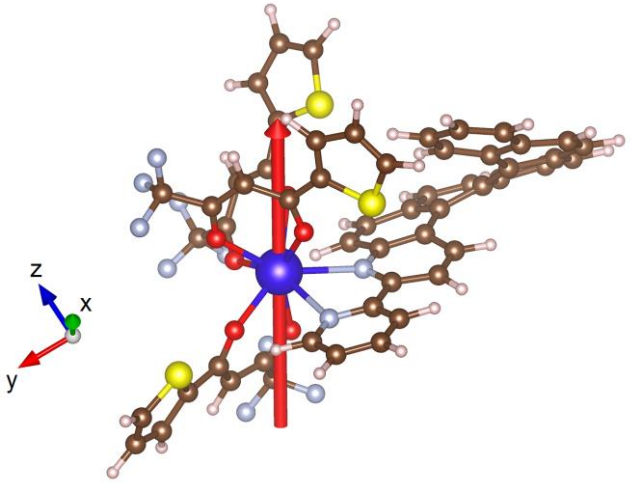


Figure 6. Representation of complex **1** with the theoretical orientation of the easy magnetic axis of the Dy^{III} center.

Moreover, magnetic relaxation pathways can be easily interpreted on the basis of magnetic transition moments (Figure 7) calculated with SINGLE_ANISO program[44-45]. It has to be pointed out that in the latter not all the contribution are included. Indeed the coupling of spin-phonon degrees of freedom in the SMM relaxation is not taken into account in the *ab initio* model whereas it has been recently evidenced its general importance.[46-47] However these discrepancies are common in literature [3][48-49] and the magnetic transition moments calculated in this work still leads to a fairly good qualitative picture. Indeed no direct transition between the two M_J states of the ground doublet or Orbach processes from the ground state are expected whereas relaxation mechanisms involving states from the third M_J state are highly probable. A non-negligible Orbach process has been found also between the second and third M_J states. The calculations indicate a difference between the calculated energy barrier ($\Delta = 82$ cm^{-1}) and the experimental barrier ($\Delta = 35$-47 cm^{-1}). However the discrepancy between these values has to be ascribed in the spin-phonon contributions mentioned above.

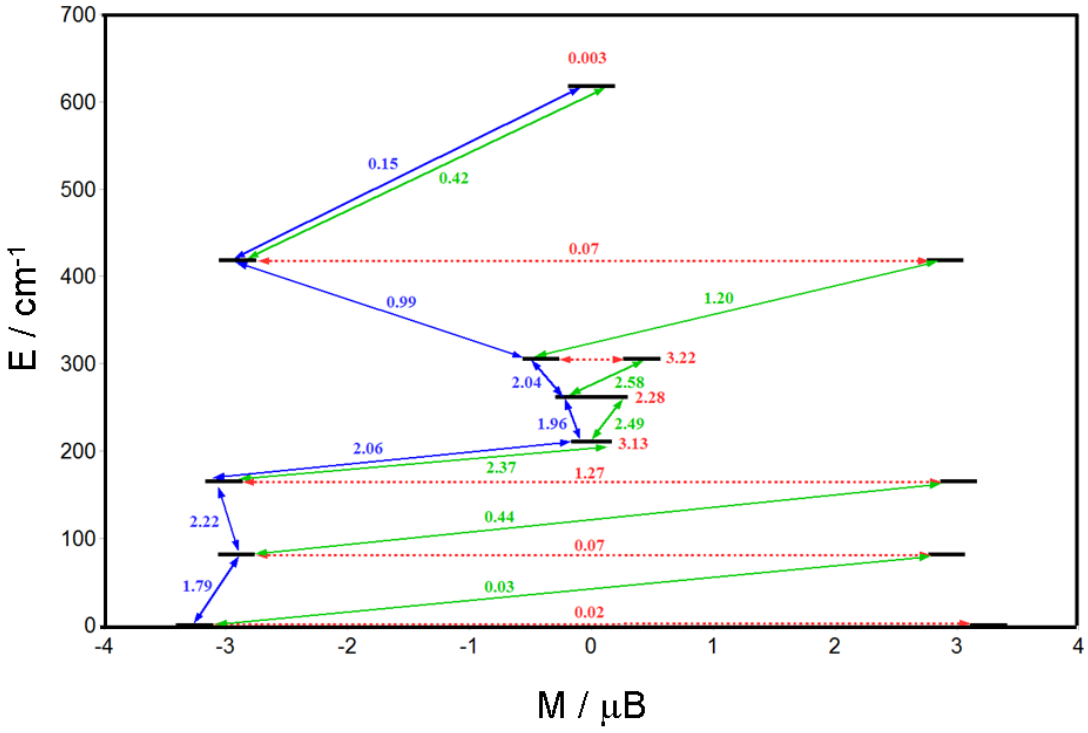


Figure 7. Computed magnetization blocking barrier in complex **1** for the Dy^{III} ion. Numbers provided on each arrow are the mean absolute values for the corresponding matrix elements of the magnetic transition dipole moment.

3. Conclusions

In the course of intermixing chirality offered by the nature of the ligands and SMM properties, we extend herein the family of [6]-helicene-based lanthanide SMM.[27] We report the synthesis of the complex [Dy(**L**)(tta)$_3$] with **L** the chiral 3-(2-pyridyl)-4-aza[6]-helicene ligand (tta^- = 2-theonyltrifluoroaacetonate). Its racemic form was structurally and magnetically characterized. [Dy(**L**)(tta)$_3$] behaves as a single molecule magnet in its crystalline phase. As expected, the substitution of $hfac^-$ ligands by tta^- moieties enhances the magnetic behavior with the opening of an hysteresis loop at 0.50 K that was only observed for the enantiopure forms in the case of [Dy(**L**)(hfac)$_3$].[27] In the near future, we will pursue our investigation of chiral lanthanide-based SMMs that may offer new perspectives in both the domains of molecular magnetism and chirality with the potential access of properties such as circularly polarized luminescence (CPL) activity that remains anecdotic for lanthanide compounds to date.

Materials and Methods

1. Synthesis. General Procedures and Materials

The precursor Dy(tta)$_3$·2H$_2$O [50] (tta^- = 2-theonyltrifluoroacetonate anion) and the ligand 3-(2-pyridyl)-4-aza[6]-helicene [39, 51] **L** were synthesized following previously reported methods. All other reagents were commercially available and used without further purification.

*2. Synthesis of complex [Dy(tta)$_3$(**L**)]·CH$_2$Cl$_2$·C$_7$H$_8$ (**1**)*

Dy(tta)$_3$·2H$_2$O (17.2 mg, 0.02 mmol) were dissolved in 5 mL of CH_2Cl_2 and then added to a solution of 5 mL of CH_2Cl_2 containing 8.3 mg of **L** (0.02 mmol). After 20 minutes of stirring, 30 mL of toluene were layered at 4°C in the dark. Slow diffusion following by slow evaporation lead to yellow

single crystals which are suitable for X-ray studies. Yield: 15.2 mg (54 % based on Dy). Anal. Calcd (%) for $C_{62}H_{40}Cl_2DyF_9N_2O_6S_3$: C 52.78, H 2.84, N 1.99; found: C 52.72, H 2.81 N, 2.09. I.R. 3426 (m), 2923 (w), 1604 (s), 1588 (m), 1566 (m), 1493 (m), 1468 (m), 1429 (m), 1256 (s), 117 (m), 1091 (w), 1046 (w), 991 (w), 963 (w), 848 (w), 815 (w), 797 (s), 773 (m), 755 (m), 654 (m), 542 (m), 503 (m) cm^{-1}.

3. Crystallography

Single crystal of $[Dy(tta)_3(\mathbf{L})]\cdot CH_2Cl_2\cdot C_7H_8$ (**1**) was mounted on a APEXII Bruker-AXS diffractometer for data collection (MoK_α radiation source, λ = 0.71073 Å). The structure was solved by direct methods using the SIR-97 program and refined with a full matrix least-squares method on F^2 using the SHELXL-97 program [1]. Crystallographic data are summarized in Table S1. Complete crystal structure results as a CIF file including bond lengths, angles, and atomic coordinates are deposited as Supporting Information. CCDC number is 1510324 for compound **1**.

4. Physical Measurements

The elementary analyses of the compound were performed at the Centre Régional de Mesures Physiques de l'Ouest, Rennes. The dc magnetic susceptibility measurements were performed on solid polycrystalline sample with a Quantum Design MPMS-XL SQUID magnetometer between 2 and 300 K in an applied magnetic field of 0.2 T for temperatures in the range 2-20 K and 1 T for temperatures between 20 and 300 K. These measurements were all corrected for the diamagnetic contribution as calculated with Pascal's constants.

5. Computational Details

Wavefunction-based calculations were carried out on molecular structures of **1** by using the SA-CASSCF/RASSI-SO approach, as implemented in the MOLCAS quantum chemistry package (versions 8.0).[52] In this approach, the relativistic effects are treated in two steps on the basis of the Douglas–Kroll Hamiltonian. First, the scalar terms were included in the basis-set generation and were used to determine the spin-free wavefunctions and energies in the complete active space self-consistent field (CASSCF) method.[53] Next, spin-orbit coupling was added within the restricted-active-space-state-interaction (RASSI-SO) method, which uses the spin-free wavefunctions as basis states.[54-55] The resulting wavefunctions and energies are used to compute the magnetic properties and g-tensors of the lowest states from the energy spectrum by using the pseudo-spin S = 1/2 formalism in the SINGLE-ANISO routine [44-45]. Cholesky decomposition of the bielectronic integrals was employed to save disk space and speed-up the calculations. [56] For **1** the active space of the self consistent field (CASSCF) method consisted of the nine 4f electrons of the Dy^{III} ion spanning the seven 4f orbitals, i.e. CAS(9,7)SCF. State-averaged CASSCF calculations were performed for all of the sextets (21 roots), all of the quadruplets (224 roots), and 300 out of the 490 doublets (due to software limitations) of the Dy^{III} ion. Twenty-one sextets, 128 quadruplets, and 107 doublets were mixed through spin−orbit coupling in RASSI-SO. All atoms were described by ANO-RCC basis sets. [57-59] The following contractions were used: [8s7p4d3f2g1h] for Dy, [4s3p2d1f] for the O and N atoms,[3s2p1d] for the C and F atoms, [4s3p1d] for the S atoms and [2s1p] for the H atoms. The atomic positions were extracted from the X-ray crystal structures. Only the position of the H and F atoms were optimized on the Y^{III} parent complexes with the Gaussian 09 (revision D.01) package [60] employing the PBE0 hybrid functional. [61] The "Stuttgart/Dresden" basis sets [62] and effective core potentials were used to describe the yttrium atom, whereas all other atoms were described with the SVP basis sets [63].

Supplementary Materials: The following are available online at www.mdpi.com/link, Figure S1: ORTEP view of **1**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms and solvent molecules of crystallization are omitted for clarity., Figure S2: Frequency dependence of the ac susceptibility components χ_M' and χ_M'' at 10 K and in zero external dc field for compound **1** with the best fitted curve with extended Debye model, Figure S3: Frequency dependence of the ac susceptibility components χ_M' and χ_M'' at 10 K and in 1000 Oe external dc field for compound **1** with the best fitted curve with extended Debye model; Figure S4: Cole-Cole plots using the ac

data performed under zero magnetic field. The black lines correspond to the fit with a generalized Debye model; Figure S5: Cole-Cole plots using the ac data performed under 1000 Oe magnetic field. The black lines correspond to the fit with a generalized Debye model; Figure S6: Magnetic hysteresis loop of **1** measured at 0.5, 1.0 and 1.5 K; Table S1: X-ray crystallographic data of **1**; Table S2: SHAPE analysis for **1**; Table S3: Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model **1** at zero field in the temperature range 2.0-15 K; Table S4: Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model **1** at 1kOe in the temperature range 1.8-5 K; Table S5: Computed energies, *g*-tensor and wavefunction composition of the ground state doublet in the effective spin ½ model for **1**.

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Author Contributions: J.-K. O. and N. S. performed the organic syntheses; F. P. performed the coordination chemistry, crystallizations, the single crystal X-ray diffraction experiments and structure refinements; O.C. performed the magnetic measurements, J. F. G. analyzed the magnetic measurements. G. F.-G., F. T. and B. L. G. performed the ab initio calculations. J. C. and L. O. discussed the results and commented on the manuscript. F.P., O.C. and B.L.G. conceived and designed the experiments and contributed equally to the writing of the article.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

SMM: Single Molecule Magnet
TTF: TetraThiaFulvalene
CH_2Cl_2: Dichloromethane
hfac: 1,1,1,5,5,5-hexafluoroacetylacetonate
tta: 2-theonyltrifluoroacetonate
PCM: Polarizable Continuum Model
CASSCF: Complete Active Space Self-Consistent Field
RASSI-SO: Restricted Active Space State Interaction – Spin-Orbit

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