

Article

Synthesis, X-Ray Crystal Structures, and Magnetic Properties of a Series of Trinuclear Rare-Earth Hepta-Chloride Clusters[†]

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[†] Dedicated to Prof. Dai-Zheng Liao on the occasion of his 85th birthday.

Abstract: Organometallic rare-earth complexes have attracted considerable attention in recent years due to their unique structures and exceptional magnetic properties. In this study, we report the synthesis and magnetic characteristics of a family of monopentamethylcyclopentadienyl-coordinated trinuclear rare-earth hepta-chloride clusters $[(\text{Li}(\text{THF})(\text{Et}_2\text{O}))(\text{Cp}^*\text{RE})_3(\mu\text{-Cl})_4(\mu_3\text{-Cl})_2(\mu_4\text{-Cl})]$ (RE_3 : RE = Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu; Cp^* = pentamethylcyclopentadienide). These clusters were synthesized by reacting LiCp^* with RECl_3 in a 1:1 molar ratio within a mixed solvent system (THF: Et_2O = 1:9), resulting in high solubility in common organic solvents such as DCM, THF, and Et_2O . Magnetic studies conducted on these paramagnetic clusters reveal the coexistence of ferromagnetic and antiferromagnetic superexchange interactions in Gd_3 . Additionally, Dy_3 exhibits both ferromagnetic and antiferromagnetic intramolecular dipolar interactions. Notably, slow magnetic relaxation was observed in Dy_3 below 23 K under a zero DC applied field with an energy barrier of $125(6) \text{ cm}^{-1}$.

Keywords: single-molecule magnet; organometallic rare-earth complex; lanthanide chloride cluster; energy barrier; exchange coupling



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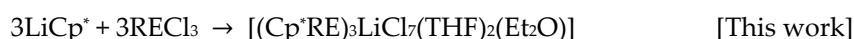
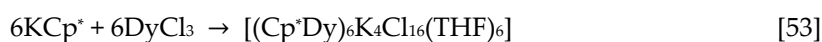
1. Introduction

Since the pioneering isolation of organometallic rare-earth complexes by Wilkinson and Birmingham in 1954 [1], the synthesis, reactivity, and physical properties of these complexes have attracted considerable attention across various fields due to the distinctive electronic structures of rare-earth ions [2–6]. Notably, significant advancements have been made in this area in recent years. For instance, cyclic multidecker sandwich rare-earth complexes have been successfully isolated and characterized [7]; metal–metal bonding, ligand–metal double bonds, and multicenter chemical bonding involving rare-earth ions have been realized [8–13]; molecular complexes featuring rare-earth ions in unconventional oxidation states (Pr(IV), Pr(V), and Tb(IV)) have been investigated [14–19]; and rare-earth telluride clusters were isolated through an efficient reduction method utilizing KC_8 [20,21]. Certain organometallic rare-earth complexes can be employed for the regio- and stereoselective hydroalkynylation of internal alkynes [22,23]. The complexes $[(\text{C}_5\text{Me}_4\text{R})\text{Eu}(\mu\text{-BH}_4)(\text{THF})_2]_2$ (R = H, Me, Ph, SiMe_3 , GeMe_3 , and $\text{P}(\text{NMe}_2)_2$) serve as potential candidates for luminescence thermometers [24,25]. Some divalent rare-earth complexes also exhibit potential as qubits [26–28]. Furthermore, several organometallic

rare-earth complexes demonstrate exceptionally high energy barriers (U_{eff}) and blocking temperatures (T_B) as single-molecule magnet (SMMs) [29–35].

SMMs have emerged as one of the most promising molecular-based advanced functional materials in recent years, owing to their capability to store information within a single molecule. This unique property positions them as leading candidates for ultra-high-density data storage [3,5]. The characteristics of SMMs are typically assessed through U_{eff} , T_B , or hysteresis temperatures (T_H). These parameters are primarily influenced by the magnetic anisotropy of spin centers and the exchange coupling between spins within the molecules [36,37]. Consequently, organometallic rare-earth complexes have opened new avenues for research into SMMs [8,12,29–35,37]. The single-ion anisotropy of lanthanide ions can be significantly enhanced by intercalating Dy(III) ions between compact aromatic rings [29–35] or by utilizing low coordination numbers [38–45]. To facilitate robust exchange couplings, radical ligands are often used to bridge lanthanide ions [46,47]. More recently, metal–metal bonding between lanthanide ions has been successfully achieved, which can also result in significant magnetic exchange coupling in truncated SMMs exhibiting ultrahard magnetism [8,12]. Moreover, the manipulation of intramolecular dipolar interactions has been successfully accomplished in dinuclear rare-earth organometallic complexes by introducing an additional Cl^- ion [48]. To further enhance the exchange couplings in lanthanide complexes, it is essential to develop a comprehensive understanding of the relationships between exchange couplings and structural characteristics [49].

The monopentamethylcyclopentadienyl-coordinated rare-earth fragments (Cp^*RE) (where Cp^* = pentamethylcyclopentadienide) are of particular interest, as they frequently serve as key components in various intriguing organometallic rare-earth complexes, including chalcogenides [20,21,50], bismuth compounds [51], and hydride clusters of rare-earth elements [52]. The starting materials employed typically consist of a mixture of KCp^* and RECl_3 , or bis- Cp^* -coordinated rare-earth complexes, or half-sandwich bis(aminobenzyl) rare-earth complexes [20,21,50–52]. We propose that mono- Cp^* -coordinated rare-earth complexes can be atomically precise and cost-effective precursors for synthesizing these clusters. Such mono- Cp^* -coordinated rare-earth complexes can be synthesized by reacting MCp^* ($\text{M} = \text{Li}, \text{Na}, \text{K}$) and RECl_3 in a 1:1 molar ratio (Scheme 1). Previous studies have demonstrated that the hexanuclear complex $[(\text{Cp}^*\text{Dy})_6\text{K}_4\text{Cl}_{16}(\text{THF})_6]$ can be synthesized using KCp^* [53]. In contrast, when NaCp^* is employed, a dimeric complex $\{\text{Na}(\mu\text{-THF})[\text{Cp}^*\text{Gd}(\text{THF})]_2(\mu\text{-Cl})_2\}$ is isolated, with $\text{Cp}^*\text{GdCl}_2(\text{THF})_3$ coexisting in the mother liquor [54]. In this study, we report on the reaction between LiCp^* and RECl_3 at a 1:1 ratio in a mixed solvent system ($\text{THF}:\text{Et}_2\text{O} = 1:9$), resulting in the formation of a family of mono- Cp^* -coordinated trinuclear rare-earth hepta-chloride clusters $[(\text{Li}(\text{THF})(\text{Et}_2\text{O}))(\text{Cp}^*\text{RE})_3(\mu\text{-Cl})_4(\mu_3\text{-Cl})_2(\mu_4\text{-Cl})]$ (RE_3 : $\text{RE} = \text{Y}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$). These clusters' structures and magnetic properties were investigated; Dy_3 emerged as a new SMM, exhibiting an energy barrier of $125(6) \text{ cm}^{-1}$.



Scheme 1. Synthesis of mono- Cp^* -coordinated rare-earth complexes through the reaction of MCp^* (where $\text{M} = \text{Li}, \text{Na}, \text{K}$) with RECl_3 in a 1:1 molar ratio.

2. Materials and Methods

2.1. Materials and Instruments

All manipulations were conducted using standard Schlenk techniques or within a glovebox under an argon atmosphere. The glassware was dried overnight at 120 °C before use. Diethyl ether (Et₂O, 99+%) (Yonghua Chemical, Changshu, China) was dried over activated alumina and stored over a potassium mirror before utilization. Anhydrous rare-earth chlorides, RECl₃, and Cp*Li, were synthesized following the established procedures from the literature [55,56]. All other reagents (AR) were procured from Energy-Chemical, (Shanghai, China) and utilized without further purification. Elemental analyses for carbon (C) and hydrogen (H) were performed using a Thermo FLASH2000 elemental analyzer (Waltham, MA, USA).

2.2. Syntheses of Complex RE₃

The clusters were synthesized through the reaction of an equimolar mixture of Cp*Li and anhydrous RECl₃, which was dispersed in a mixed solvent (THF: Et₂O = 1:9). The resulting mixture was stirred overnight at room temperature. After filtration, the precipitate LiCl (a byproduct) was removed, followed by the evaporation of the solvent under vacuum. The residue was then dissolved in 5 mL of Et₂O. Finally, the slow volatilization of Et₂O yielded crystals of RE₃ suitable for X-ray diffraction after one day, with yields of approximately 25% for RE = Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, based on anhydrous RECl₃. The elemental analyses calculated (found) the following for C₄₂H₇₁Cl₇Ln₃LiO₃: **Y₃**: C, 43.99 (43.60); H, 6.20 (6.16); **Gd₃**: C, 37.31 (37.50); H, 5.26 (5.31); **Tb₃**: C, 37.17 (37.21); H, 5.24 (5.24); **Dy₃**: C, 36.88 (36.68); H, 5.20 (5.51); **Ho₃**: C, 36.68 (36.84); H, 5.17 (5.46); **Er₃**: C, 36.50 (36.45); H, 5.14 (5.44); **Tm₃**: C, 36.37 (36.15); H, 5.12 (5.42); **Yb₃**: C, 36.10 (36.23); H, 5.09 (5.39); and **Lu₃**: C, 36.16 (36.27); H, 5.09 (5.10).

2.3. Crystal Structure Determination

Single-crystal X-ray diffraction (SXRD) studies were conducted using Bruker D8 Venture (Mo K α radiation (λ = 0.71073 Å)) (Bruker, Berlin, Germany) at 100 K for RE₃ (where RE = Gd, Ho–Lu, and Y), and at 200 K for Tb₃ and Dy₃. Using Olex2 (v1.5), the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using least squares minimization [57–59]. All hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms, with displacement parameters also dependent on the parent carbon atom U_{eq} value. The Cambridge Crystallographic Data Centre contains the crystal structures under the following CCDC numbers: 2441413 (Gd₃), 2441414 (Tb₃), 2441415 (Dy₃), 2441416 (Ho₃), 2441417 (Er₃), 2441418 (Tm₃), 2441419 (Yb₃), 2441420 (Lu₃), and 2441421 (Y₃). Crystal data and structure refinement are summarized in Table S1.

2.4. Magnetic Measurements

Crushed polycrystalline samples were sealed with melted eicosane in an NMR tube under vacuum for magnetic measurements. Magnetic susceptibilities were measured with a Quantum Design MPMS-3 SQUID magnetometer (Quantum Design, San Diego, CA, USA) between 2 and 300 K.

2.5. Ab Initio Calculations

OpenMolcas [60] (version: v21.06) was employed to conduct the CASSCF-SO calculations of the electronic structures of Dy₃, utilizing molecular geometries derived from crystallographic analyses. No optimization was performed except for selecting the largest disorder component. Relativistic effects were incorporated using the second-order Douglas–

Kroll–Hess Hamiltonian, and basis sets from the ANO-RCC library were utilized accordingly [61,62]. Specifically, VTZP quality basis sets were applied for Dy atoms, VDZP quality for coordinating C and Cl atoms, and VDZ quality for all other atoms. To conserve disk space and reduce computational demands, the Cholesky decomposition of two-electron integrals was executed with a threshold set at 10^{-8} . The state-averaged CASSCF orbitals corresponding to sextets, quartets, and doublets were optimized with 21, 224, and 490 states, respectively, through the RASSCF module. For constructing and diagonalizing the spin-orbit (SO) coupling Hamiltonian using the RASSI module, 21 sextets, 128 quartets, and 130 doublets were selected. The resulting spin-orbit wavefunctions were decomposed into their corresponding crystal field (CF) wavefunctions. Subsequently, the ground atomic multiplet, associated tensors, energy barrier, and principal magnetic axes for each Dy(III) ion were calculated using SINGLE_ANISO [63]. Additionally, POLY_ANISO was utilized to compute dipolar interactions within Dy_3 [64,65].

3. Results and Discussion

3.1. Syntheses and Structural Characterization

All title RE_3 compounds were synthesized using a consistent procedure, wherein equimolar amounts of Cp^*Li and RECl_3 were dispersed in a mixed solvent ($\text{THF}:\text{Et}_2\text{O} = 1:9$) and stirred overnight at room temperature. The byproduct LiCl precipitated out and was subsequently separated by filtration. Notably, the products obtained after solvent removal under vacuum exhibited high solubility in common organic solvents, including DCM, THF, and Et_2O . Single crystals suitable for X-ray diffraction studies were acquired through the slow evaporation of saturated Et_2O solutions of these complexes at room temperature within a glove box.

As revealed by X-ray diffraction, the nine RE_3 isostructural compounds crystallized in the same orthorhombic noncentrosymmetric space group $Pmn21$ (Table S1). The cluster-type molecule (Figure 1a) for RE_3 consists of three $\{\text{Cp}^*\text{RE}\}$ units, one Li^+ , seven Cl^- , and three coordinated solvent molecules, which include two THF and one Et_2O . The three $\{\text{Cp}^*\text{RE}\}$ fragments and the Li^+ ion are interconnected by four $\mu_2\text{-Cl}$, two $\mu_3\text{-Cl}$, and one $\mu_4\text{-Cl}$ (Figure 1b), resulting in a distorted heterometallic tetrahedron (Figure 1c). The $\mu_4\text{-Cl}$ ion is situated within a seesaw-type polyhedron formed by four metal ions, which have been documented in a limited number of rare-earth clusters [66–70]. It is noteworthy that the structures of these clusters bear resemblance to $[\text{Cp}^*\text{LuCl}_2]_3[\text{LiCl}(\text{THF})_2]$, which was identified as a byproduct during the activation of white phosphorus with organometallic rare-earth complexes [66]. The primary distinction lies in the coordination environments of the Li^+ ions. In this study's RE_3 complex, the Li^+ ion at the vertex of $[\text{Cp}^*\text{RE}]_3$ is coordinated to one Et_2O molecule and one disordered THF molecule. In contrast, it is coordinated with two THF molecules in $[\text{Cp}^*\text{LuCl}_2]_3[\text{LiCl}(\text{THF})_2]$.

All three RE(III) ions in RE_3 are capped by a Cp^* , with RE1 and RE1# coordinated to five Cl^- ligands, while RE2 is associated with four Cl^- ligands and one oxygen atom from THF. The distances between the RE and Cl bonds, ranging from 2.54 Å to 3.00 Å (Tables S2–S10), align well with those reported for other RE–Cl compounds [49,50,53,54]. Similarly, the distances of the RE–C bonds fall within the range of 2.54–2.68 Å (Tables S2–S10), and the distances from the RE(III) ions to the centroid of the coordinated Cp^* rings vary from 2.31 Å to 2.36 Å (Tables S2–S10). These measurements also correspond closely with previously documented values for RE– Cp^* complexes [47–54]. The three RE ions are interconnected through three bridging Cl atoms, resulting in an interionic distance ranging from 3.92 Å to 4.05 Å (Table S11). Notably, it should be mentioned that RE1 and RE1# are bridged by two $\mu_3\text{-Cl}$ ligands and one $\mu_4\text{-Cl}$ ligand; conversely, either pair consisting of (RE1 and RE2) or (RE1# and RE2) is connected via one $\mu_2\text{-Cl}$ ligand

along with one μ_3 -Cl ligand and one μ_4 -Cl ligand. This distinction results in slightly longer interionic distances for the former case than those observed in the latter. Furthermore, in terms of coordination geometry, the Cp* ligands attached to [RECl₃RE] units (Figure 2a) adopt a ‘cis conformation’ in cases involving both RE1 and RE1#, whereas they exhibit a ‘trans conformation’ when considering pairs such as (RE1 and RE2) or (RE1# and RE2). This variation may influence different magnetic exchange couplings, as discussed further below.

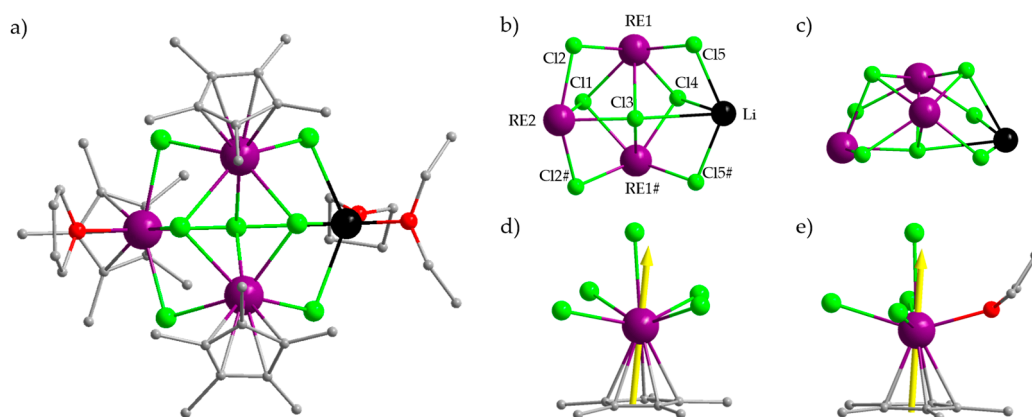


Figure 1. Ball-and-stick representations of RE_3 (a) and side views of the RE_3Cl_7 core within RE_3 (b,c). The local coordination environments for RE1 (d) and RE2 (e) in RE_3 are illustrated. The yellow arrows indicate the principal magnetic axes of the ground doublets derived from CASSCF-SO calculations for Dy_3 . The color code is as follows: violet, RE; green, Cl; grey, C; and red, O. H atoms are omitted for clarity. Symmetry codes are as follows: #, 1 – x , + y , + z .

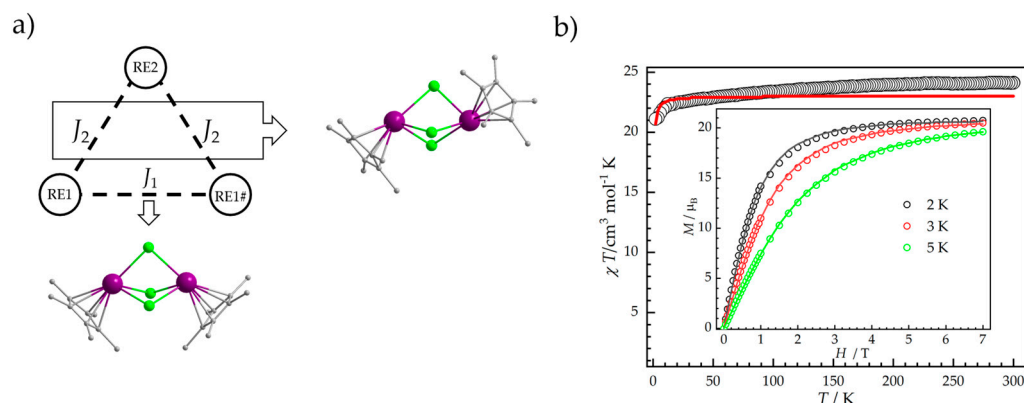


Figure 2. (a) The two types of intramolecular magnetic interactions of RE_3 with the corresponding [RECl₃RE] units coordinated to Cp* ligands. The symmetry codes are as follows: #, 1 – x , + y , + z . (b) The χT versus T plot for Gd_3 under a 1000 Oe DC field. Inset: the field-dependent magnetization plots at indicated temperatures. The solid lines are the best fits.

3.2. Static-Field Magnetic Susceptibilities for RE_3

To assess the static magnetic properties and intramolecular magnetic interactions in RE_3 , we measured the static-field magnetic susceptibilities under an applied DC field of 1000 Oe across a temperature range of 2–300 K. Additionally, field-dependent magnetic susceptibilities were recorded up to 7 T at low temperatures (Figures 2b and 3). The static-field magnetic susceptibilities for RE_3 exhibited remarkably similar trends (Figures 2b and 3). The experimental χT values at 300 K closely align with the expected values for the corresponding RE(III) ions (Table 1) [71,72]. The decrease in χT values upon cooling for RE_3 (RE = Tb–Yb) can be attributed to the thermal depopulation of Stark levels, anisotropy effects, and/or antiferromagnetic interactions [71,72]. Furthermore, the maximum magnetic moment observed at 2 K and 7 T for Gd_3 corresponds well with the saturation value of

$7 \mu_B$ per Gd(III) ion. In contrast, the experimental values for the other RE₃ compounds (RE = Tb–Yb) are significantly lower than their respective saturation values, indicating a pronounced anisotropy associated with these complexes.

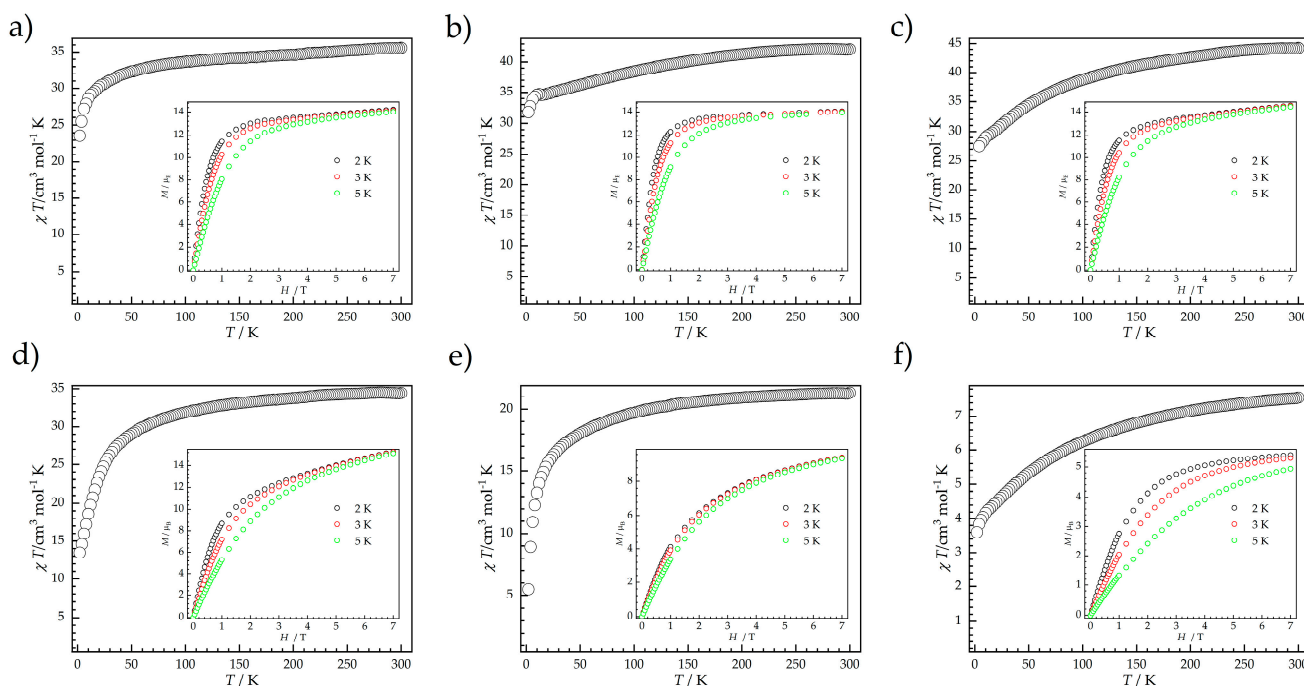


Figure 3. The χT versus T plot for (a) Tb₃, (b) Dy₃, (c) Ho₃, (d) Er₃, (e) Tm₃, and (f) Yb₃ under a 1000 Oe DC field. Inset: the field-dependent magnetization plots at indicated temperatures.

Table 1. The total spin momentum (S), total orbit momentum (L), total angular quantum number (J), and g values for the ground states of free RE(III) ions [71,72], χT values, and magnetic moments per RE(III) ion in RE₃.

RE(III)	S	L	J	g	χT Value (cm ³ mol ^{−1} K)			Magnetic Moments (μ_B)	
					Expected	Experimental		Saturated	Experimental
						300 K	300 K		
Gd	7/2	0	7/2	2	7.87	8.04	7.03	7	6.92
Tb	3	3	6	3/2	11.82	11.86	7.86	9	4.74
Dy	5/2	5	15/2	4/3	14.17	14.03	10.59	10	4.69
Ho	2	6	8	5/4	14.07	14.75	9.17	10	4.86
Er	3/2	6	15/2	6/5	11.48	11.48	4.49	9	5.09
Tm	1	5	6	7/6	7.15	7.11	1.83	7	3.14
Yb	1/2	3	7/2	8/7	2.57	2.52	1.20	4	1.80

Using the PHI program (version 3.1.6), the intramolecular magnetic interactions in Gd₃ can be assessed by fitting the temperature- and field-dependent magnetic susceptibilities [73]. As previously mentioned, two types of ‘conformations’ correspond to the different magnetic exchange couplings in Gd₃ (Figure 2a). Consequently, the Hamiltonian expressed as $\hat{H} = -2J_1(\hat{S}_{Gd1} \cdot \hat{S}_{Gd1\#}) - 2J_2(\hat{S}_{Gd1} \cdot \hat{S}_{Gd2} + \hat{S}_{Gd1\#} \cdot \hat{S}_{Gd2})$ is employed to describe these magnetic exchange couplings. Here, J_1 represents the super-exchange constant for the interaction between Gd1 and Gd1#, while J_2 pertains to the interactions involving either Gd1 with Gd2 or Gd1# with Gd2. The super-exchange constants (J_1 and J_2) derived from

this Hamiltonian indicate a ferromagnetic exchange coupling when the value is positive ($J > 0$). Conversely, an antiferromagnetic exchange coupling can be identified if the value is negative. As illustrated in Figure 2b, the optimal fits (solid lines) combined with a variable g -factor in the Zeeman Hamiltonian and the isotropic exchange Hamiltonian mentioned above yielded values of $J_1 = 6.14 \times 10^{-3} \text{ cm}^{-1}$, and $J_2 = -1.29 \times 10^{-2} \text{ cm}^{-1}$ with $g = 1.97$ for Gd_3 . Such weak superexchange interactions among Gd(III) ions are not particularly surprising given that the 4f electrons are confined within contracted 4f orbitals and superexchange interactions mediated by non-radical ligands tend to exhibit inherently weak characteristics [50,51,74].

3.3. Dynamic Magnetic Susceptibilities for Dy_3

The dynamic magnetic properties of RE_3 were examined through AC magnetic susceptibilities measured under a zero applied field at low temperatures (Figures S1–S6). Notably, only Dy_3 exhibited slow magnetic relaxations at these low temperatures, likely attributable to the capacity of Cp^* ligands to effectively enhance the single-ion anisotropy of Dy(III) ions. The frequency-dependent AC susceptibilities under a zero applied field were subsequently collected from 2 K to 23 K (Figure 4) and fitted using the generalized Debye model (Figure S7), yielding relaxation times and corresponding α parameters (Table S12). [36,75,76]. The α parameters range from 0.3 to 0.5, indicating a relatively wide distribution of relaxation times. This variation may arise from the differing coordination environments of Dy1 and Dy2 (Figure 1d,e) within Dy_3 and the trimer interactions [74].

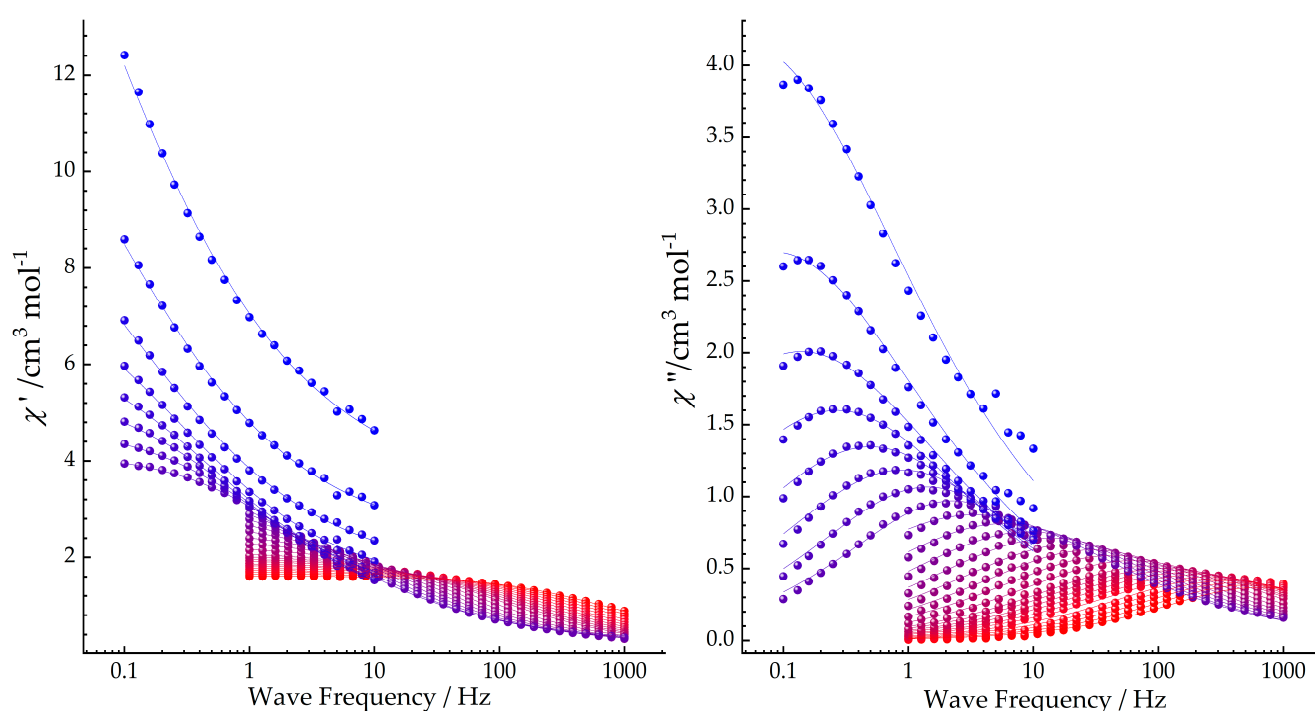


Figure 4. The in-phase (χ' , left) and out-of-phase (χ'' , right) frequency-dependent AC susceptibility signals for Dy_3 under a zero DC field, measured from 2 K (blue) to 23 K (red). The solid lines represent the best fit according to the generalized Debye model.

As illustrated in Figure 5a, the relaxation profiles ($\ln(\tau)$) for Dy_3 exhibit a rapid increase with rising values of $1/T$ when $1/T$ is less than 0.1 (corresponding to temperatures above 10 K). Subsequently, this increase slows down, ultimately reaching a nearly temperature-independent regime at $1/T = 0.5$ (at a temperature of 2 K). The log-log version for the plot of the magnetic relaxation rate versus the temperature for Dy_3 (inset in Figure 5a) indicates that the Raman process (the linear part) is dominated in the temperature range

of 4–15 K [76]. Thus, the relaxation profiles for **Dy**₃ can be fitted with Equation (1), which combines the Orbach process (U_{eff} is the effective energy barrier, and τ_0 is the attempt frequency of the Orbach process), the Raman process (CT^n), and the quantum tunneling of magnetization (QTM) process (τ_{QTM}). The parameters obtained are as follows: $U_{\text{eff}} = 125(6) \text{ cm}^{-1}$, $\tau_0 = 1.4(5) \times 10^{-7} \text{ s}$, $C = 1.5(3) \times 10^{-3} \text{ s}$, $n = 4.2(1)$ and $\tau_{\text{QTM}} = 3.1(2) \text{ s}$. The U_{eff} is lower than the calculated energy gap between the first excited Kramers doublets, and the ground states for the Dy(III) ions in **Dy**₃, probably because of the significant contribution of the Raman process to the magnetic relaxations up to 23 K (inset in Figure 5a) and a strong QTM.

$$\tau^{-1} = \tau_0^{-1} \exp(-U_{\text{eff}}/T) + CT^n + \tau_{\text{QTM}}^{-1} \quad (1)$$

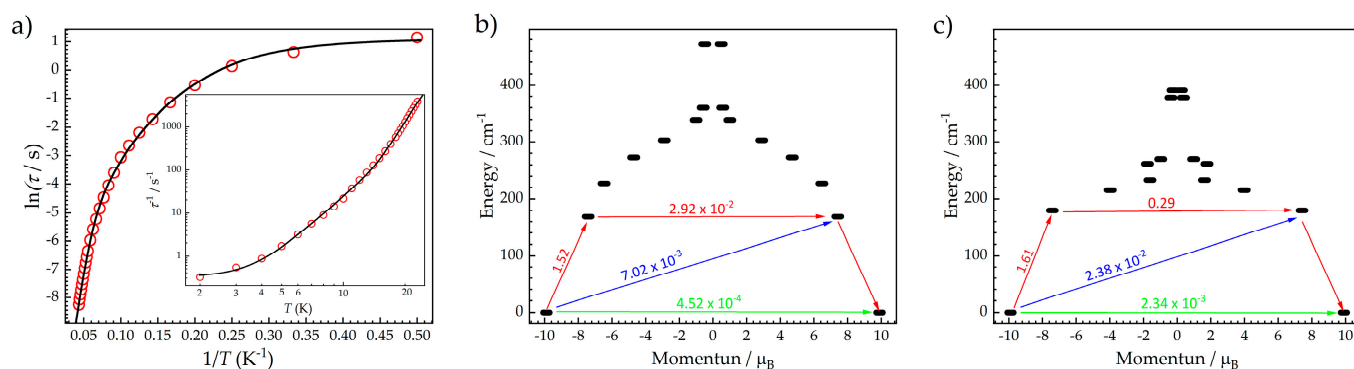


Figure 5. The $\ln(\tau)$ vs. $1/T$ plots for **Dy**₃ (inset: log–log version for plot of the magnetic relaxation rate versus the temperature for **Dy**₃) (a). The solid lines best fit with Equation (1), including the Orbach, Raman, and QTM processes. The electronic states from the CASSCF-SO calculations for Dy1 (b) and Dy2 (c) in **Dy**₃. The thick black lines represent the Kramers doublets as a function of their magnetic moment along the magnetic axis. The red arrows represent the most probable relaxation pathway for the Orbach process. The green lines correspond to the QTM through the ground states. The blue line represents the off-diagonal relaxation process. The numbers at each arrow represent the mean absolute value of the corresponding matrix element of the transition magnetic moment.

3.4. Ab Initio Calculations for **Dy**₃

The electronic states of the Dy(III) ions in **Dy**₃ were studied with *OpenMolcas* by complete active space self-consistent field spin–orbit (CASSCF-SO) calculations (Table S13) [60]. For both Dy1 and Dy2 in **Dy**₃, the ground states are predominantly characterized by the most magnetic component of $m_J = \pm 15/2$, accounting for over 98%. In contrast, the excited states exhibit various magnetic components (see Tables 2 and 3). The energy gaps between the first excited Kramers doublets and the ground states are 169 cm^{-1} for Dy1 and 180 cm^{-1} for Dy2 (Figure 5b,c). The principal magnetic axes of the ground Kramers' doublets obtained are oriented along the centroid of the coordinated Cp* ring relative to the Dy(III) ion (Figure 1d,e). This orientation indicates that the single-ion anisotropy of the Dy(III) ion is predominantly influenced by the Cp*[−] ligand, while THF and Cl[−] exhibit a similar effect on the single-ion anisotropy of the Dy(III) ion.

The intramolecular dipolar interactions, which play an essential role for the low temperature magnetic property of polynuclear complexes [48,49,77–79], can be calculated accurately using the program POLY_ANISO [63,64]. As shown in Figure 6a, the calculated principal magnetic axes for Dy1 and Dy1# in **Dy**₃ are oriented along the Dy– μ_4 –Cl direction and the Dy– μ_3 –Cl direction for Dy2. For Dy1 and Dy1#, the principal magnetic axes are in-plane crossed (Figure 6b), while the principal magnetic axes are out-of-plane crossed for Dy1 and Dy2 or Dy1# and Dy2 (Figure 6c). Such arrangements of the principal magnetic axes cannot minimize the transversal component of the intramolecular dipolar field, so the QTM in **Dy**₃ remains strong, as mentioned above [48,49,77–79]. The dipolar interaction

between Dy1 and Dy1# is antiferromagnetic with an exchange constant of -0.92 cm^{-1} , which is ferromagnetic with an exchange constant of 0.39 cm^{-1} for Dy1 and Dy or Dy1# and Dy2. These values are close to the dipolar interactions in other polynuclear Dy(III) complexes [65].

Table 2. The electronic structure of Dy1 in **Dy₃** was calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet. Other components with low contributions are not displayed.

Energy (cm ⁻¹)	g1	g2	g3	Wavefunction
0.00	1.04×10^{-3}	1.67×10^{-3}	19.81	$98.9\% \pm 15/2 \rangle \dots$
168.911	6.26×10^{-2}	9.52×10^{-2}	17.64	$58.2\% \pm 13/2 \rangle + 14.5\% \pm 11/2 \rangle + 14.5\% \pm 9/2 \rangle + 7.9\% \pm 7/2 \rangle \dots$
227.038	1.60×10^{-2}	2.86×10^{-2}	14.49	$37.3\% \pm 13/2 \rangle + 17.1\% \pm 9/2 \rangle + 16\% \pm 11/2 \rangle + 16\% \pm 7/2 \rangle \dots$
273.431	3.53	4.72	10.07	$48.1\% \pm 11/2 \rangle + 16.8\% \pm 5/2 \rangle + 13.3\% \pm 7/2 \rangle + 10.8\% \pm 3/2 \rangle \dots$
302.717	2.56	5.62	10.56	$42.8\% \pm 9/2 \rangle + 18.8\% \pm 7/2 \rangle + 11.9\% \pm 11/2 \rangle + 10.8\% \pm 3/2 \rangle \dots$
338.500	0.14	2.65	13.20	$30.6\% \pm 5/2 \rangle + 25.8\% \pm 1/2 \rangle + 25.6\% \pm 7/2 \rangle + 8.1\% \pm 9/2 \rangle \dots$
360.075	0.56	1.97	14.98	$39.1\% \pm 3/2 \rangle + 20.2\% \pm 5/2 \rangle + 16.1\% \pm 1/2 \rangle + 10.9\% \pm 7/2 \rangle \dots$
472.122	2.36×10^{-2}	3.85×10^{-2}	19.77	$42.9\% \pm 1/2 \rangle + 28.9\% \pm 3/2 \rangle + 15.6\% \pm 5/2 \rangle + 7.5\% \pm 7/2 \rangle \dots$

Table 3. The electronic structure of Dy2 in **Dy₃** was calculated with the crystal field parameters obtained from CASSCF-SO at the crystal structure. Each row corresponds to a Kramers doublet. Other components with low contributions are not displayed.

Energy (cm ⁻¹)	g1	g2	g3	Wavefunction
0.00	6.24×10^{-3}	9.61×10^{-3}	19.84	$99.5\% \pm 15/2 \rangle \dots$
180.303	0.80	0.85	16.23	$73.3\% \pm 13/2 \rangle + 8.8\% \pm 5/2 \rangle + 5.8\% \pm 11/2 \rangle + 5.6\% \pm 7/2 \rangle \dots$
214.563	10.20	7.12	2.75	$31.6\% \pm 9/2 \rangle + 23.4\% \pm 11/2 \rangle + 11.2\% \pm 3/2 \rangle + 10.7\% \pm 13/2 \rangle \dots$
233.352	0.68	4.13	8.94	$31.4\% \pm 11/2 \rangle + 21.6\% \pm 7/2 \rangle + 11.9\% \pm 9/2 \rangle + 10.6\% \pm 13/2 \rangle \dots$
261.853	10.85	7.67	1.04	$46.8\% \pm 7/2 \rangle + 42.4\% \pm 9/2 \rangle + 4.3\% \pm 5/2 \rangle + 3.3\% \pm 11/2 \rangle \dots$
270.398	8.77	5.42	0.48	$44.4\% \pm 5/2 \rangle + 30.6\% \pm 11/2 \rangle + 16.9\% \pm 3/2 \rangle + 3.6\% \pm 13/2 \rangle \dots$
378.250	0.58	2.73	14.23	$53\% \pm 3/2 \rangle + 32.6\% \pm 5/2 \rangle + 5\% \pm 1/2 \rangle + 4.5\% \pm 7/2 \rangle \dots$
390.606	0.39	3.26	15.02	$68.9\% \pm 1/2 \rangle + 11.5\% \pm 7/2 \rangle + 8.8\% \pm 9/2 \rangle + 8.2\% \pm 3/2 \rangle \dots$

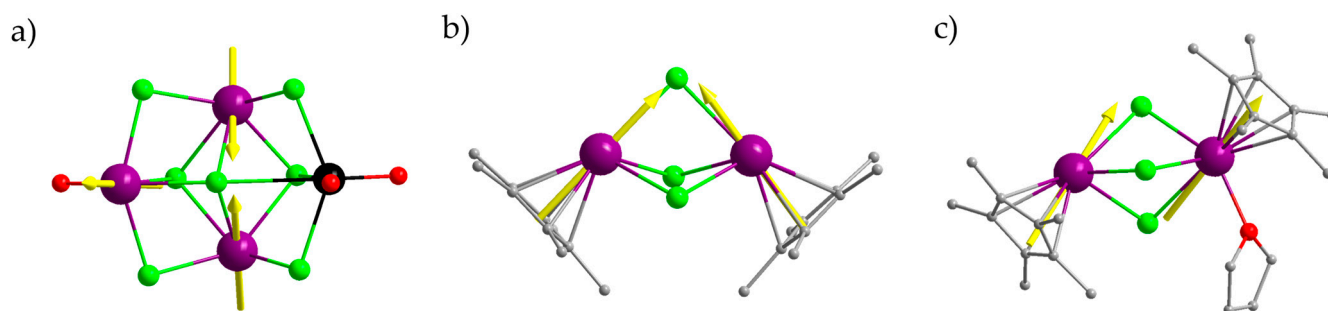


Figure 6. Arrangements of the principal magnetic axes for **Dy₃** (a), for Dy1 and Dy1# (b), for Dy1 and Dy2 or Dy1# and Dy2 (c). The yellow arrows represent the principal magnetic axes of the ground doublets obtained from the CASSCF-SO calculations.

4. Conclusions

The synthesis, structure determinations, magnetic properties, and electronic structures of novel trinuclear rare-earth hepta-chloride clusters were reported. These mono-Cp*-coordinated rare-earth complexes obtained by the reaction of LiCp* and RECl₃ in a 1:1 ratio

can serve as starting materials for more interesting organometallic rare-earth clusters due to their high solubility in common organic solvents. Complex **Dy₃** is a novel single-molecule magnet that exhibits a significant contribution from the Orbach process, the Raman process, and QTM. The energy barrier of 125(6) cm^{−1} is primarily attributed to the single-ion anisotropy associated with its Dy(III) ions. Further magnetic studies indicate that the ‘*cis* conformation’ of the Cp* ligands coordinated to the [RECl₃RE] units results in ferromagnetic superexchange interactions in **Gd₃**, while it leads to antiferromagnetic intramolecular dipolar interactions in **Dy₃**. Conversely, the ‘*trans* conformation’ exhibits opposing effects. It remains unclear how the ligands control the exchange interactions. The investigation into the control of exchange interactions in molecular magnetic materials is ongoing, which may pave the way for the development of more advanced molecular magnetic materials.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/magnetochemistry11050038/s1>. Table S1: Crystal data and structure refinement for **RE₃** (RE=Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y); Table S2–S10: Selected bond distances (Å) for **Gd₃**, **Tb₃**, **Dy₃**, **Ho₃**, **Er₃**, **Tm₃**, **Yb₃**, **Lu₃** and **Y₃**; Table S11: Selected RE–RE distances (Å) for **RE₃**; Table S12: Relaxation fitting parameters obtained using a generalized Debye model for **Dy₃** from 23 K to 2 K under zero DC field; Table S13: Ab initio calculated crystal field parameters (B_q^k) for Dy1 and Dy2 in **Dy₃**; Figures S1–S6: Temperature-dependence of the in-phase (χ' , top) and out-of-phase (χ'' , bottom) AC susceptibility signals under zero DC field by standard AC susceptibility measurements for **Tb₃**, **Dy₃**, **Ho₃**, **Er₃**, **Tm₃** and **Yb₃** at indicated frequencies; Figure S7: Cole–Cole plots using the frequency-dependence AC susceptibility data under the zero DC field for **Dy₃** from 2 K (blue) to 23 K (red). The solid lines are the best fits.

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