Carbonate-Bridged Lanthanoid Triangles: Single Molecule Magnet Behavior, Inelastic Neutron Scattering and *Ab Initio* Studies

*Marcus J. Giansiracusa,[†] Michele Vonci,[†] Willem Van den Heuvel,[†] Robert W. Gable,[†]
Boujemaa Moubaraki,[‡] Keith S. Murray,[‡] Dehong Yu,[§] Richard A. Mole,[§] Alessandro
Soncini^{*†} and Colette Boskovic^{*†}*

School of Chemistry, University of Melbourne, Victoria, 3010, Australia; School of
Chemistry Monash University, Clayton, 3800, Australia; Bragg Institute, Australian Nuclear
Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW, 2232,
Australia.

[†] University of Melbourne.

[‡] Monash University

[§] Bragg Institute

Abstract

Optimization of literature synthetic procedures has afforded in good yield, homogeneous and crystalline samples of five analogs $\text{Na}_{11}[\{\text{RE}(\text{OH}_2)\}_3\text{CO}_3(\text{PW}_9\text{O}_{34})_2]$ (**1-RE**, RE = Y, Tb, Dy, Ho and Er). Phase transfer methods have allowed isolation of mixed salts $(\text{Et}_4\text{N})_9\text{Na}_2[\{\text{RE}(\text{OH}_2)\}_3\text{CO}_3(\text{PW}_9\text{O}_{34})_2]$ (**2-RE**, RE = Y and Er). The isostructural polyanions in these compounds are comprised of a triangular arrangement of trivalent rare earth ions bridged by a μ_3 -carbonate ligand and sandwiched between two trilacunary Keggin $\{\text{PW}_9\text{O}_{34}\}$ polyoxometalate ligands. Alternating current magnetic susceptibility studies of **1-Dy**, **1-Er** and **2-Er** reveal the onset of frequency-dependence in the out-of-phase susceptibility in the presence of an applied magnetic field at the lowest measured temperatures. Inelastic neutron scattering spectra of **1-Ho** and **1-Er** exhibit transitions between the lowest lying crystal field (CF) split states of the respective $J = 8$ and $15/2$ ground spin-orbit multiplets of the Ho(III) and Er(III) ions. Complementary *ab initio* calculations performed for these two analogs allow excellent reproduction of the experimental magnetic susceptibility and low temperature magnetization data and are in reasonable agreement with the experimental INS data. The *ab initio* calculations reveal that the slight difference in coordination environments of the three lanthanoid(III) ions in each complex gives rise to differences in the CF splitting that are not insignificant. This theoretical result is consistent with the observation of multiple relaxation processes by ac magnetic susceptibility and the broadness of the measured INS peaks. The *ab initio* calculations also indicate substantial mixing of the M_J contributions to the CF split energy levels of each lanthanoid(III) ion. Calculations indicate that the CF ground states of the Ho(III) centers in **1-Ho** are predominantly comprised of contributions from small M_J , while those of the Er(III) centers in **1-Er** are predominantly comprised of contributions from large M_J , giving rise to slow

magnetic relaxation. Although no direct evidence for intramolecular RE...RE magnetic coupling is observed in either magnetic or INS studies, on the basis of the *ab initio* calculations we find non-collinear magnetic axes in **1-Er** that are co-planar with the Er-triangle, and radially arranged with respect to the triangle's centroid, thus we argue that the absence of magnetic coupling in this system arises from dipolar and antiferromagnetic superexchange interactions that cancel each other out.

INTRODUCTION

Reported in 2003, terbium and dysprosium bis(phthalocyanine) complexes were the first lanthanoid species identified as single-molecule magnets (SMMs).^{1,2} Since that discovery, lanthanoid-based SMMs (Ln-SMMs) have been found to exhibit slow magnetic relaxation at much higher temperatures than are accessible with SMMs based on d-block metals, as well as providing important new insights into magnetization quantum tunneling.³⁻⁷ The slow magnetization relaxation results from the large unquenched orbital angular momentum of trivalent lanthanoid ions, which, interacting with the ligand environment, results in a sizeable CF splitting of the spin-orbit coupled J states, often with dominant contributions from large M_J values in the ground state inducing an energy barrier to magnetization reversal.⁸ The phenomenological energy barrier to magnetization reversal (U_{eff}) is typically obtained from an Arrhenius plot of relaxation times derived from variable frequency and temperature alternating current (ac) magnetic susceptibility measurements. Lanthanoid SMMs can exhibit substantial energy barriers as a result of CF splitting, with the current record energy barrier of 938 K (Arrhenius pre-exponential factor $\tau_0 = 1.2 \times 10^{-11}$ s) reported for a heteroleptic bis(phthalocyanine) terbium complex.⁹ Indeed, the majority of Ln-SMMs are still based on dysprosium and terbium.

Correlation of the measured U_{eff} with the energy splitting of the M_J levels and the structural features of the trivalent lanthanoid center remains an important task for understanding the structural origin of SMM properties and ultimately designing new SMMs. A powerful, but relatively underutilized experimental technique for precisely determining the energy splitting of the M_J levels, is inelastic neutron scattering (INS). INS provides a direct probe of the energy levels, allowing accurate mapping of the energy separation of the lowest lying energy levels of Ln(III) ions. Nevertheless, INS has been relatively little employed in

the investigation of Ln-SMMs.¹⁰⁻¹⁴ This is in part because the large neutron absorption cross section of dysprosium hinders the measurement of dysprosium compounds, in addition the typically large CF splitting of Dy SMMs gives rise to INS allowed transitions outside of the typical dynamic range of cold neutron spectrometers. Complementary to experimental investigations is theoretical modelling, with the *ab initio* Complete Active Space Self Consistent Field (CASSCF) computational strategy, originated by Roos *et al.* and developed by Chibotaru and Ungur,^{15,16} proving very useful for modelling the electronic structure of many Ln-SMMs.^{17,18}

An alternative to organic ligands for Ln-SMMs are inorganic polyoxometalates (POMs),¹⁹ as defect or lacunary POMs are excellent multidentate oxygen donor ligands for trivalent lanthanoids. Advantages offered by POM ligands include minimization of unwanted intermolecular interactions by the steric bulk of the POM, the accessibility of nuclear spin-free isotopes to reduce quantum tunneling, the provision of coordination geometries and crystal fields that are unavailable with organic ligands.²⁰⁻²⁴ The highest energy barrier to magnetization reversal for a POM-supported Ln-SMM is $U_{\text{eff}} = 73$ K, reported by Mizuno and coworkers for a complex containing two rare earth ions sandwiched between two dilacunary Keggin POMs.^{25,26} This complex was achieved through chemical manipulation of the coordination geometry of the lanthanoid centers to generate a six-coordinate distorted trigonal prismatic environment. The achievement of this energy barrier was particularly interesting as the precursor complex with seven-coordinate geometry for the lanthanoid centers was not a SMM.

Of potential interest as SMMs are the $[\{\text{RE}(\text{OH}_2)\}_3\text{CO}_3(\text{A}-\alpha\text{-XW}_9\text{O}_{34})_2]^{n-}$ (RE = rare earth) family. A number of analogs have been reported with X = P, As, Si and Ge and both early and late lanthanoids, as well as yttrium, typically as salts with mixed cations.²⁷⁻³⁵ The complexes all contain three seven-coordinate rare earth ions bridged by a μ_3 -carbonate

ligand. Recently, ac magnetic susceptibility studies of a dysprosium analog of this family formulated as $\text{K}_{8-n}\text{H}_{3-n}[\text{Dy}_{3-n}\text{K}_n(\text{H}_2\text{O})_3(\text{CO}_3)(\text{A-}\alpha\text{-AsW}_9\text{O}_{34})(\text{A-}\beta\text{-AsW}_9\text{O}_{34})]$ revealed field-induced SMM behavior with $U_{\text{eff}} = 53 \text{ K}$.³² The prospect of tuning the SMM behavior by removal of the seventh aqua ligand of the lanthanoid centers is appealing. Also of interest is the possibility of the triangular arrangement of lanthanoid centers leading to a non-collinear arrangement of the magnetic moments in the ground Kramers doublet (KD), and potentially resulting in a toroidal moment in the ground state. This has been observed previously in a trinuclear dysprosium complex, where the easy axes of magnetization for each dysprosium(III) ion are almost coplanar with the Dy-triangle and oriented along a tangential direction.³⁶⁻³⁹ This results in an apparent non-magnetic ground state, which should be impossible for an odd number of Kramers ions, such as dysprosium(III). Herein we report the synthesis and study of the family $\text{Na}_{11}[\{\text{RE}(\text{OH}_2)\}_3\text{CO}_3(\text{PW}_9\text{O}_{34})_2]$ (**1-RE**) for RE = Y, Tb, Dy, Ho and Er, including a detailed elucidation of the magnetic behavior and electronic structure by magnetic and INS measurements and *ab initio* calculations.

EXPERIMENTAL SECTION

Synthesis. Materials and methods: All chemicals were of reagent grade and used as received. The precursor POM, $\text{Na}_8\text{H}[\text{PW}_9\text{O}_{34}]$ was prepared following the literature procedure.⁴⁰ The compound was air dried to avoid solid state isomerization and verified by IR spectroscopy.

$\text{Na}_{11}[\{\text{Y}(\text{OH}_2)\}_3\text{CO}_3(\text{PW}_9\text{O}_{34})_2]$ (1-Y**).** Solid $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (0.24 g, 0.80 mmol) was dissolved in water (10 ml) and a solution of Na_2CO_3 (1 ml, 1 M) was added dropwise with stirring to give a pH of 6.1. The mixture was heated to 80 °C and then $\text{Na}_8\text{H}[\text{PW}_9\text{O}_{34}]$ (1.0 g, 0.42 mmol) was added quickly with vigorous stirring. The mixture was stirred for an hour at 80 °C then allowed to cool to room temperature. Insoluble material was removed by

centrifugation and NaCl (0.79 g, 14 mmol) was added to the solution. The sample was left to stand to yield colorless hexagonal-faced rod-shaped crystals that were isolated by vacuum filtration and washed with chilled dilute NaCl solution. A single crystal X-ray structural analysis of the wet crystals identified the presence of 42 molecules of solvent water, indicating the formulation to be **1-Y**·42H₂O, while the air-dried sample partially dehydrated affording **1-Y**·35H₂O. Yield: 400 mg, 33 %. Anal calcd (found) for **1-Y**·35H₂O, Na₁₁CH₇₆Y₃P₂O₁₀₉W₁₈: H 1.33 (1.36), C 0.21 (0.27), Na 4.42 (4.30) %. Selected IR data (KBr, cm⁻¹): 3443 (s), 1623 (m), 1479 (m), 1070 (s), 1015 (m), 945 (m), 917 (m), 832 (m), 790 (s), 706 (m), 504 (w). ³¹P NMR (162 MHz, D₂O) δ = -10.56 ppm; ¹³C NMR (100 MHz, D₂O/acetone) δ = 171.6 ppm.

Na₁₁[{Y(OH₂)₃CO₃(PW₉O₃₄)₂]·35H_xD_{2-x}O (1-Y^D). A sample of **1-Y** was dried under vacuum at 100 °C then was recrystallized from 1 M NaCl solution in D₂O. The degree of deuteration was determined by attenuated total reflectance (ATR) infrared spectroscopy to be around 50 %.

Na₁₁[{RE(OH₂)₃CO₃(PW₉O₃₄)₂] (1-Tb, 1-Dy, 1-Ho, 1-Er) The RE = Tb, Dy, Er and Ho analogues were obtained following analogous procedures as for **1-Y**, using the appropriate RECl₃ salt. All crystals have the same hexagonal-faced rod morphology. Crystals of **1-RE**·xH₂O for single crystal X-ray structural analysis were kept in contact with mother liquor to prevent loss of water molecules of hydration. All compounds had similar cell parameters, and similar chemical analyses after air drying, and so the structural analyses proceeded on the basis of all compounds including the same amount of solvent water.

Na₁₁[{Tb(OH₂)₃CO₃(PW₉O₃₄)₂] (1-Tb). The procedure for **1-Y** was slightly modified, with 8 ml of water used initially and then the pH adjusted to 6.1 using 0.5 M NaOH. Yield: 110 mg (9 %) of hexagonal rod-like colorless crystals. The wet crystals and air-dried sample were identified as **1-Tb**·42H₂O and **1-Tb**·35H₂O, respectively. Anal Calcd

(found) for **1-Tb**·35H₂O, Na₁₁CH₇₆Tb₃P₂O₁₀₉W₁₈: H 1.28 (1.20), C 0.20 (0.26), Na 4.05 (4.20) %. Selected IR data (KBr, cm⁻¹): 3441 (s), 1619 (m), 1469 (m), 1065 (s), 1013 (m), 944 (m), 915 (m), 830 (m), 787 (s), 697 (m), 509 (w).

Na₁₁[{Dy(OH₂)₃CO₃(PW₉O₃₄)₂] (1-Dy). Synthesized as per **1-Y**. Yield: 400 mg (32 %). The wet crystals and air-dried sample were identified as **1-Dy**·42H₂O and **1-Dy**·35H₂O, respectively. Anal Calcd (found) for **1-Dy**·35H₂O, Na₁₁CH₇₆Dy₃P₂O₁₀₉W₁₈: H 1.28 (1.43), C 0.20 (0.25), Na 4.05 (4.25) %. Selected IR data (KBr, cm⁻¹): 3442 (s), 1627 (m), 1474 (m), 1067 (s), 1013 (m), 944 (m), 917 (m), 831 (m), 786 (s), 700 (m), 510 (w).

Na₁₁[{Ho(OH₂)₃CO₃(PW₉O₃₄)₂] (1-Ho). Synthesized as per **1-Tb**. Yield: 330 mg (25 %) of yellow/pink crystals. The wet crystals and air-dried sample were identified as **1-Ho**·42H₂O and **1-Ho**·35H₂O, respectively. Anal Calcd (found) for **1-Ho**·35H₂O, Na₁₁CH₇₆Ho₃P₂O₁₀₉W₁₈: H 1.28 (1.26), C 0.20 (0.28), Na 4.25 (5.10) %. Selected IR data (KBr, cm⁻¹): 3443 (s), 1619 (m), 1473 (m), 1070 (s), 1016 (m), 945 (m), 919 (m), 830 (m), 789 (s), 698 (m), 505 (w).

Na₁₁[{Ho(OH₂)₃CO₃(PW₉O₃₄)₂]·35H_xD_{2-x}O (1-Ho^D). Synthesized as per **1-Y^D**.

Na₁₁[{Er(OH₂)₃CO₃(PW₉O₃₄)₂] (1-Er). Synthesized as per **1-Y**. Yield: 160 mg (13 %) of pink crystals. The wet crystals and air-dried sample were identified as **1-Er**·42H₂O and **1-Er**·35H₂O, respectively. Anal Calcd (found) for **1-Er**·35H₂O, Na₁₁CH₇₆Er₃P₂O₁₀₉W₁₈: H 1.28 (1.38), C 0.20 (0.20), Na 4.24 (4.25). Selected IR data (KBr, cm⁻¹): 3454 (s), 1624 (m), 1480 (m), 1069 (s), 1015 (m), 945 (m), 918 (m), 830 (m), 788 (s), 703 (m), 511 (w).

Na₁₁[{Er(OH₂)₃CO₃(PW₉O₃₄)₂]·35H_xD_{2-x}O (1-Er^D). Synthesized as per **1-Y^D**.

(Et₄N)₉Na₂[{Er(OH₂)₃CO₃(PW₉O₃₄)₂]·16H₂O (2-Er). Compound **1-Er** (120 mg, 0.02 mmol) was dissolved in water (2 ml) and a separate solution of Hept₄NBr (106.8 mg, 0.22 mmol) in toluene (2 ml) was prepared. The two solutions were vigorously shaken in a separating funnel and the pink color transferred into the upper organic layer. The toluene

layer was separated and dried over MgSO_4 . The solution was then filtered and a solution of Et_4NBr (46.2 mg, 0.22 mmol) in MeCN (4 ml) was layered over the toluene solution, with an intervening "buffer" layer of MeCN (3 ml) to yield a microcrystalline solid. Yield: 36 mg, 22 %. Anal Calcd (found) for **2-Er**, $\text{Na}_2\text{C}_{73}\text{H}_{218}\text{N}_9\text{Er}_3\text{P}_2\text{O}_{90}\text{W}_{18}$: H 3.31 (3.35), C 13.32 (13.5), N 1.92 (1.9), Na 0.7 (< 0.6) %. Selected IR data (KBr, cm^{-1}): 3424 (s), 2983 (w), 2951 (w), 1638 (m), 1534 (w), 1483 (s), 1457 (m), 1393 (m), 1174 (m), 1065 (s), 1009 (m), 943 (s), 917 (m), 892 (m), 825 (m), 782 (s), 709 (m), 514 (w).

(Et₄N)₉Na₂[{Y(OH₂)₃CO₃(PW₉O₃₄)₂]}·15H₂O (2-Y). Synthesized as per **2-Er**. Yield: 25 mg, 15 %. Anal Calcd (found) for **2-Y**, $\text{Na}_2\text{C}_{73}\text{H}_{216}\text{N}_9\text{Y}_3\text{P}_2\text{O}_{89}\text{W}_{18}$: H 3.41 % (3.40), C 13.85 (14.36), N 1.99 (2.00), Na 0.73 (< 0.6) %. Selected IR data (KBr, cm^{-1}): 3424 (s), 2983 (w), 2950 (w), 1638 (m), 1531 (w), 1483 (s), 1459 (m), 1393 (m), 1174 (m), 1065 (s), 1008 (m), 943 (s), 917 (m), 893 (m), 827 (m), 783 (s), 712 (m), 513 (w). ³¹P NMR (162 MHz, D₂O) δ -10.74 ppm; ¹³C NMR (100 MHz, D₂O) δ = 7.33 (CH₃) and 52.64 (CH₂) ppm; ¹H NMR (400 MHz, D₂O) δ = 3.15 ppm (q, 2H), 1.15 ppm (t, 3H).

X-Ray Data Collection and Structure Solution. The crystallographic data for compounds **1-RE**· $x\text{H}_2\text{O}$, (RE = Y, Tb Dy, Ho and Er, Table 1) were collected at 130 K using an Agilent Technologies SuperNova Dual Wavelength single crystal X-ray diffractometer using Cu- $K\alpha$ radiation (λ = 1.5418 Å). Crystals were transferred directly from mother liquor to oil in order to prevent solvent loss. The data were reduced using CrysAlis^{Pro} software (Version 1.171.37.34, 1.171.36.20 or 1.171.35.21) using empirical absorption correction with spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm, or numerical absorption correction based on Gaussian integration over a multifaceted crystal model. The structures were solved using direct methods in SHELXL-97 and refined using a full-matrix least squares procedure based on F^2 . During the refinement process for **1-Y**·42H₂O, electron density peaks of up to 7 eÅ⁻³ could not be assigned. The peaks were associated with disorder

in the crystal as they appeared equidistant to all W atoms in the structure. This is evidence of twinning along the crystallographic a axis in the crystal used for data collection, which results in the high R_{int} and R_1 values obtained for this structure.

Table 1. Crystallographic data for compounds **1-RE**·42H₂O

	1-Y ·42H ₂ O	1-Tb ·42H ₂ O	1-Dy ·42H ₂ O	1-Ho ·42H ₂ O	1-Er ·42H ₂ O
Formula	Na ₁₁ CH ₈₄ Tb ₃ P ₂ O ₁₁₆ W ₁₈	Na ₁₁ CH ₈₄ Tb ₃ P ₂ O ₁₁₆ W ₁₈	Na ₁₁ CH ₈₄ Dy ₃ P ₂ O ₁₁₆ W ₁₈	Na ₁₁ CH ₈₄ Ho ₃ P ₂ O ₁₁₆ W ₁₈	Na ₁₁ CH ₈₄ Er ₃ P ₂ O ₁₁₆ W ₁₈
Formula weight					
/ g mol ⁻¹	5843.54	6053.57	6064.31	6071.60	6078.59
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	17.3425(4)	17.3863(2)	17.3861(1)	17.3187(1)	17.3703(2)
<i>b</i> / Å	25.9777(4)	26.0413(2)	26.0478(1)	25.9772(2)	26.0440(2)
<i>c</i> / Å	23.4294(4)	23.4293(2)	23.4180(1)	23.3379(2)	23.4126(3)
<i>α</i>	90	90	90	90	90
<i>β</i>	111.680(2)	111.602(1)	111.6424(7)	111.488(1)	111.668(1)
<i>γ</i>	90	90	90	90	90
<i>V</i> / Å ³	9808.7(3)	9862.9(2)	9857.7(1)	9769.7(1)	9843.3(2)
<i>Z</i>	4	4	4	4	4
<i>T</i> / K	130.0(1)	130.0(1)	130.0(1)	130.0(1)	135(7)
ρ_{calc} / g cm ⁻³	3.878	4.00	4.008	4.05	4.023
μ / mm ⁻¹	22.98	49.99	51.596	44.32	44.235

reflns measd	84999	69343	68519	70066	71768
unique reflns	23420	19554	19888	19743	20109
Data / restraints / parameters	23420 / 13 / 781	19554 / 33 / 1346	19888 / 24 / 1316	19743 / 1 / 1353	20109 / 24 / 1301
R_{int}	0.1014	0.0512	0.0467	0.0353	0.0333
$R_1 [I > 2\sigma(I)]$	0.0667	0.0315	0.0326	0.028	0.0314
wR_2 (all data)	0.1909	0.0723	0.0792	0.0677	0.0756
Goodness-of-fit on F^2	1.066	1.066	1.045	1.131	1.139
$\Delta\rho_{\max,\min} / e \text{ \AA}^{-3}$	7.01/-5.23	2.62/-1.43	2.96/-1.76	1.94/-2.34	2.50/-1.81

Magnetic Measurements. Magnetic Measurements were performed on a Quantum Design MPMS-XL SQUID magnetometer. The samples were restrained in Vaseline and **1-Y·35H₂O** was measured and subtracted as a diamagnetic correction for the other samples of **1-RE·35H₂O**.

Other Measurements. Infrared spectra (KBr disk) were recorded on a Bruker Tensor 27 FTIR spectrometer. Elemental analyses were performed at Campbell Microanalytical Laboratory, University of Otago. Multinuclear ¹H, ¹³C and ³¹P NMR spectra were acquired in D₂O (or D₂O with 1 % acetone) on a Varian MR400 spectrometer referenced to H₂O, acetone and H₃PO₄, respectively. Thermogravimetric analyses were performed on a Mettler Toledo thermal analyzer using a ramp rate of 10 °C per minute up to a maximum temperature of 1000 °C.

Inelastic Neutron Scattering (INS). Inelastic neutron scattering experiments were performed using the cold neutron time-of-flight spectrometer PELICAN at the Bragg Institute, Australian Nuclear Science and Technology Organisation (ANSTO).⁴¹ Coarsely ground powder samples of **1-Y^D**, **1-Ho^D** and **1-Er^D** of mass 1.5 g were placed in an annular aluminium can with a 1 mm gap, chosen to give a 10 % scatter and thus minimize multiple scattering. The sample can was mounted in a top-loading CCR type cryostat and the sample cooled. The instrument is equipped with a PG002 monochromator, this was aligned to give 4.74 Å neutrons which afforded a resolution of 135 µeV at the elastic line. All filters were removed from the beam and the higher orders removed by phasing the choppers. Data were also collected using 2.37 Å by rephasing the choppers to only allow $\lambda/2$ (i.e. using the PG004 reflection), this configuration had a resolution of 0.5 meV. In both configurations the master and slave choppers were operated at 100 Hz. The neutrons were scattered by the sample and detected using the 1 m high detectors that span 125 degrees. The data were binned in time to give 1000 equal time channels per pulse. Data were normalized to a vanadium standard and

the inherent instrument background corrected by subtracting an empty sample can and then converted to $S(Q,\omega)$. All data processing and manipulations were performed using standard procedures and the Large Array Manipulation Program (LAMP).⁴² Data were collected with both neutron wavelengths at 5, 10, 20, 50 or 80 K for **1-Ho^D** and **1-Er^D**, while for **1-Y^D** the data were collected at 5 and 50 K.

***Ab Initio* Calculations.** For lanthanoid-containing complexes, the lowest lying molecular states are dominated by the ground atomic multiplet of the lanthanoid(III) ion, the energies of which are split (and wavefunctions mixed) by the CF potential produced by the ligands in the full molecule. This multiplet is approximately described by a single LS term, where L and S are the total orbital and spin angular momenta of the 4f electrons. This term is strongly split by spin orbit coupling into spin-orbit multiplets characterized by a total angular momentum quantum number J , which, in the ground state, couples L and S for more (less) than half filled shell into the maximal (minimal) achievable total angular momentum $J = L + S$ ($J = |L - S|$). However, any *ab initio* attempt at computing the true nature of the degenerate ground state in a lanthanoid(III) complex should of course take into account the fact that spin-orbit coupling can couple more LS terms, and not limit itself to split the ground LS term only.

Due to the complex multiplet structure of many-electron atoms, and the strong spin-orbit coupling, *ab initio* approaches are computationally demanding, as first the molecular orbitals must be optimized for all the different spin states that can be achieved by distributing n 4f electrons in fourteen 4f spin-orbitals (also counting MS states, these are in principle $\text{binomial}(14,n)$). This was achieved using the well-known CASSCF *ab initio* methodology¹⁶ as implemented in the quantum chemistry software Molcas 8.0.⁴³⁻⁴⁶ Once such states and their molecular orbitals are optimized, it is necessary to diagonalize the spin-orbit operator in this space. Following optimization of the different spin states for a set of CF split LS terms,

the state interaction module of the same program was employed to subsequently diagonalize a mean-field spin-orbit operator in the basis of the optimized spin states to obtain the final CF levels.⁴⁷ Finally, the Single Aniso module of Molcas was used to compute the magnetic properties of the molecule (susceptibility and magnetization) and, only for **1-Er**, to evaluate the *g*-tensor principal components and axes for the ground KD and the decomposition of the *ab initio* wavefunction into M_J total angular momentum components, with total angular momentum ($J = 15/2$) quantized along the principal magnetic axis of the ground KD, according to a well-established procedure.¹²

Work on the trinuclear **1-RE** series was undertaken using a double zeta (DZ) description of the rare earth atom and near neighbors, with further atoms described by a minimal basis set. The use of *ab initio* model potential (AIMP) basis sets was necessary for the calculations, due to the large number of heavy atoms present in the POM ligands. The twelve tungsten atoms connecting coordinated O atoms were described using an AIMP basis set with the recommended basis description (W.ECP.Casarrubios.13s10p9d5f.3s3p4d2f.12e-CG-AIMP.). The remaining tungsten positions were described using the minimal AIMP description (W.ECP.Casarrubios.13s10p9d5f.1s2p2d1f.12e-CG-AIMP.). The two inactive rare earth sites were described using an AIMP for Y(III) ions (Y.ECP.Barandiaran.11s8p7d.1s2p2d.9e-CG-AIMP.). The use of a Cholesky vector approximation to the calculation of the two-electron Coulomb repulsion integrals was also employed with a threshold of 10^{-8} . Despite the pseudo D_{3h} point symmetry of the molecule, the calculations employed the strict C_1 molecular point symmetry determined by single crystal X-ray diffraction and did not include cations or solvent.

In order to correlate calculations with the observed INS spectra, the single ion properties were individually calculated across the three lanthanoid sites, then, assuming

negligible exchange coupling between ions, the results were combined to give an overall description.

As the hydrogen atoms were not observed experimentally by X-ray crystallography, chemically intuitive positions for the hydrogen atoms of the aqua ligands were utilized. In the crystal structure, two of the aqua ligands exhibit intramolecular electrostatic interactions with sodium cations through lone pairs of electrons, which facilitates estimation of the hydrogen positions.

Results and Discussion

Syntheses. The experimental procedures reported here to obtain the sodium salts **1-RE** are adapted from the previously described methods of Khoshnavazi *et al.*, which in many cases afforded mixed salts with sodium, potassium and/or ammonium countercations.²⁷⁻³⁵ Some variation in the procedure was necessary across the lanthanoid series to obtain homogeneous crystalline samples. The synthesis involved the dropwise addition of excess Na₂CO₃ to an aqueous solution containing the RECl₃ with stirring. The pH was measured and adjusted to 6.1 using a small amount of NaOH where necessary for some rare earth metals (Tb and Ho). Polyoxometalate synthesis is extremely pH sensitive and a pH of 6.1 is required to form the target complexes. The necessity for selective pH adjustment likely reflects a small degree of impurity in some of the RECl₃ precursors. The solution was then heated to 80 °C followed by the addition of Na₈H[A- α -PW₉O₃₄] with vigorous stirring, in a stoichiometric 2:3 ratio with the rare earth. After heating for an hour, the solution was cooled to room temperature followed by centrifugation to remove insoluble material. The addition of an excess of sodium chloride to the clear solution ensures crystallization of compounds with the full complement of eleven sodium countercations, rather than partially protonated species.

Some samples (Tb and Y) required recrystallization from a 1.5 M NaCl solution in order to obtain crystals suitable for single crystal X-ray structural analysis. All compounds were isolated as pure crystalline samples in low to moderate yield. While the highest yields were achieved for Y and Dy, attempts made to adapt the procedure to isolate a Gd analog did not afford a homogeneous product.

In order to explore the effect on the magnetic properties of changing the coordination environment of the lanthanoid(III) ions by removing the aqua ligands, we attempted to synthesize organo-soluble salts of $[\{RE(OH_2)\}_3CO_3(PW_9O_{34})_2]^{11-}$, with a view to removal of aqua ligands following the procedure employed for polyanions such as $[SiW_{11}Co(H_2O)O_{39}]^{6-}$.⁴⁸ Analogs of **1-Er** were explored as the pink color facilitates monitoring the progress of the reactions. Efforts to access such salts initially involved direct precipitation with tetraalkylammonium cations from the reaction solution, which afforded the sodium salts because of the presence of excess sodium. Addition of tetraalkylammonium cations to **1-RE** redissolved in water did not give a precipitate and it was not possible to isolate tetraalkylammonium salts from these solutions. We then turned to a general method reported by Cronin *et al.*,⁴⁹ which involves stirring an aqueous solution of the POM with Bu_4NBr and MeCN, followed by acidification to pH 1.5 and then work-up of the oily layer that forms. Efforts following this procedure with **1-Er** instead gave $Na_3[PW_{12}O_{40}]$, as the target compound is unstable at the lower pH required for this method. Finally we reverted to the long standing method of phase transfer and after surveying several transfer agents and solvents,^{48, 50-52} we found that tetraheptylammonium bromide in toluene worked well. Layering the resulting toluene solution with tetraethylammonium bromide in acetonitrile afforded a microcrystalline sample of the mixed tetraethylammonium/sodium salt, which however is insoluble in organic solvents. As the phase transfer step was successful, we also attempted evaporation of the tetraheptylammonium-containing toluene solution prior to

addition of tetraethylammonium, followed by redissolution in dry dichloromethane and stirring overnight with molecular sieves in an effort to remove the aqua ligands on the erbium centers.⁴⁸ After evaporation of the solvent, the infrared spectrum of the residue indicated the loss of integrity of the POM structure.

Structure Description. The crystal data for compounds **1-RE**·42H₂O are presented in Table 1. Compounds **1-RE**·42H₂O (RE = Y, Tb, Dy and Er) crystallize in the monoclinic space group $P2_1/n$. The measurement of several crystals from different batches confirms that compound **1-Ho**·42H₂O alone crystallizes in the monoclinic space group $P2_1/c$. Each compound contains one complete polyanion within the asymmetric unit, together with sodium cations and water molecules of hydration. All POMs are isostructural, with the different space group for **1-Ho**·42H₂O associated with different crystal packing relative to the crystallographic axes.

Figure 1. Combined polyhedral and ball and stick representation of $[\{\text{RE}(\text{OH}_2)\}_3\text{CO}_3(\text{PW}_9\text{O}_{34})_2]$. Color code: WO_6 octahedra, yellow; RE, grey, P, pink; C, black; O, red; aqua ligands, cyan.

The RE-POMs in **1-RE** are comprised of two trilacunary Keggin $\{A-\alpha-PW_9O_{34}\}$ units sandwiching a planar triangular arrangement of rare earth(III) ions bridged by a $\mu_3-\eta^2:\eta^2:\eta^2$ -carbonate ligand (Figure 1). Compound **1-Tb**·42H₂O showed evidence of disorder in the trilacunary POMs, with around 5 % occupancy of an isomeric $\{A-\beta-PW_9O_{34}\}$ unit assigned for the three rotated W atoms. The RE-POM is strictly asymmetric, but has approximate D_{3h} point symmetry, with the pseudo-threefold axis passing through the carbonate carbon and the two phosphorus atoms. The rare earth centers are seven-coordinate with a terminal aqua ligand in addition to four μ_2 -oxo ligands and bonds to two of the oxygen atoms from the μ_3 -carbonate. Use of program SHAPE 2.1,⁵³ which calculates continuous shape measures of a set of points relative to the vertices of ideal reference polyhedra, indicates that the local rare earth coordination geometry is closest to monocapped trigonal prismatic. The SHAPE indices range from 1.05 to 1.93 for monocapped trigonal prismatic, where an index of zero indicates no distortion from the ideal geometry, while the SHAPE indices calculated for all other ideal 7-vertex reference polyhedral are higher (Table S1). The coordination environment becomes less distorted across the series as the central ion decreases in ionic radius. The interatomic parameters of the rare earth(III) ions (Table 2) exhibit the usual trends associated with the decrease in ionic radii across the series and are consistent with those previously reported for related $[\{RE(OH_2)\}_3CO_3(XW_9O_{34})_2]^{n-}$ POMs.²⁷⁻³⁵ These bonds and angles are also of similar magnitude to those observed in other non-POM complexes with $\mu_3-\eta^2:\eta^2:\eta^2$ -carbonate ligands bridging three RE(III) centers, such as $[Dy_6(ovph)_4(Hpvph)_2Cl_4(H_2O)_2(CO_3)_2]$ (ovph = *o*-vanillin picolinoylhydrazone), the so-called lanthaballs $[Ln_{13}(H_2O)_6(phen)_{18}(ccnm)_6(CO_3)_{14}]$ (phen = 1,10-phenanthroline, ccnm = carbamoylcyanonitrosomethanide (C(CN) (CONH₂)(NO)⁻), $[\{Ln(LH_2)(H_2O)Cl\}_3(CO_3)]^{4+}$ (L = a tetraiminodiphenolate macrocyclic ligand) and $[Ln_6Zn_2(CO_3)_5(OH)(H_2L)_4(H_3L)_2(H_4L)]^+$ (L = polydentate N/O-donor ligand).^{54, 55}

Table 2. Selected interatomic distances (Å) and angles (°) for **1-RE**·42H₂O

	1-Y	1-Tb	1-Dy	1-Ho	1-Er
Distances					
RE–O _{oxo}	2.227(10)- 2.27(1)	2.252(5)- 2.301(7)	2.245(5)- 2.297(5)	2.232(4)- 2.282(4)	2.225(3)- 2.277(5)
RE–O _{carbonate}	2.40(1)- 2.44(1)	2.425(6)- 2.438(6)	2.416(6)- 2.433(5)	2.414(4)- 2.425(4)	2.402(5)- 2.422(4)
RE–O _{aqua}	2.39(1)- 2.45(1)	2.400(6)- 2.461(6)	2.394(5)- 2.454(5)	2.380(5)- 2.448(5)	2.370(5)- 2.432(5)
RE···RE	4.827(2)- 4.840(2)	4.8459(7)- 4.8611(7)	4.8327(6)- 4.8531(6)	4.8285(7)- 4.8386(6)	4.8034(6)- 4.8297(6)
Angles (carbonate oxygens)					
O-RE-O	54.6(3)- 54.9(4)	54.3(2)- 55.3(2)	54.6(2)- 54.6(2)	54.6(1)- 54.9(2)	55.0(2)- 55.1(2)
RE-O-RE'	174.4(5)- 175.3(5)	173.8(3)- 174.6(3)	174.0(3)- 174.8(2)	174.5(2)- 174.9(2)	174.4(2)- 175.5(2)

The compounds **1-RE**·42H₂O (RE = Y, Tb, Dy and Er) are isomorphous, while **1-Ho**·42H₂O crystallizes in a different space group and with a slightly smaller unit cell (Table 1). For all five compounds, sodium countercations are closely associated with both bridging and terminal oxo ligands from the POM, as well as water molecules of crystallization. The crystal packing (Figure S1) observed for **1-RE**·42H₂O (RE = Y, Tb, Dy and Er) involves an alternating layers with molecules in the same layer oriented in one direction and molecules in the adjacent layers in a different direction. The POM ligands ensure the RE atoms are well separated between molecules with the closest intramolecular RE···RE distance around 7 Å. The crystal packing for **1-Ho**·42H₂O (Figure S2) is similar, although along different crystallographic directions.

Thermogravimetric Analysis. Thermogravimetric analysis (Figure S3) of **1-RE**·35H₂O (RE = Y, Tb, Dy, Ho and Er) indicate a consistent degree of hydration across the **1-RE** series ranging from around 8 to 11 % mass loss up to 200 °C, which is consistent with 35 hydrate molecules. Decomposition of the μ_3 -carbonate ligand is observed around 500 °C, which is consistent with literature reports of carbonate ligand decomposition in the range 460-480 °C for related [$\{\text{RE}(\text{OH}_2)\}_3\text{CO}_3(\text{A-}\alpha\text{-XW}_9\text{O}_{34})_2$]ⁿ⁻ and similar complexes.^{27, 32, 34, 35} The **2-Y** and **2-Er** samples exhibit almost identical profiles, with around 4 % mass loss attributed to hydrate molecules. The organic cations decompose between 200 and 470 °C to give an overall loss of 21.1 and 20.4 % for **2-Y** and **2-Er**, respectively. A subsequent loss of approximately 1 %, observed around 700 °C is attributed to decomposition of the central carbonate ligand, which occurs at higher temperatures when there are fewer sodium cations in the crystal lattice.

Infrared and NMR Spectroscopy. The infrared spectra of **1-RE**·35H₂O (RE = Y, Tb, Dy, Ho and Er) and **2-RE** (RE = Y and Er) all exhibit a set of features (Figure S4) that can be attributed to the common RE-POM. The spectra are similar to those previously reported for the [$\{\text{RE}(\text{OH}_2)\}_3\text{CO}_3(\text{XW}_9\text{O}_{34})_2$]ⁿ⁻ family.²⁷⁻³⁴ A band around 1479 cm⁻¹ is assigned to the doubly degenerate ν_3 -carbonate stretch.²⁷ A pair of bands around 1070 and 1015 cm⁻¹ are ν_3 vibrations associated with the phosphate units within the Keggin structure.²⁷ Fingerprint bands associated with the POM backbone are observed in the range 400-1000 cm⁻¹. The band at 945 cm⁻¹ is due to the terminal W=O stretch, while bands at 917 and 832 cm⁻¹ arise from corner-shared bridging O-W-O stretching vibrations and bands at 790 and 706 cm⁻¹ arise from edge-shared bridging O-W-O stretches.⁵⁶

The ³¹P NMR spectra of both **1-Y** and **2-Y** in D₂O (Figure S5) exhibit a single resonance, consistent with a single phosphotungstate polyanion in solution. The chemical shifts of -10.6 and -10.7 ppm for **1-Y** and **2-Y**, respectively, are consistent with previous

reports for the $[\{\text{RE}(\text{OH}_2)\}_3\text{CO}_3(\text{PW}_9\text{O}_{34})_2]^{11-}$ family.²⁷⁻³⁰ The chemical shifts for the parent Keggin plenary phosphotungstate $[\text{PW}_{12}\text{O}_{40}]^{3-}$ and lacunary $[\text{PW}_9\text{O}_{34}]^{9-}$ are -14.9 and -6.6 ppm, respectively.^{57, 58} The spectrum for **1-Y** remains unchanged over a period of 2 weeks, indicating stability of the complex in solution. The ^{13}C NMR spectrum measured for **1-Y** (Figure S6) also shows a single resonance at 171.6 ppm due to the carbonate ligand. This is also consistent with literature spectra.²⁷⁻³⁰ Unfortunately, **2-Y** was insufficiently soluble to observe this resonance, even with an almost saturated sample run overnight.

Magnetic Measurements. Direct current (dc) magnetic susceptibility data measured with a 1 and 10 kOe applied field between 2 and 300 K for **1-Ln**·35H₂O (Ln = Tb, Dy, Ho and Er) and **2-Er** are presented in Figure 2 and magnetization data measured at 2 K with fields up to 50 kOe are presented in Figure S7. Data measured for **1-Y**·35H₂O were employed as the diamagnetic correction for the paramagnetic analogs. The 300 K $\chi_M T$ values of 35.3, 42.9, 40.9, 33.7 and 33.5 cm³ mol⁻¹ K measured for **1-Tb**·35H₂O, **1-Dy**·35H₂O, **1-Ho**·35H₂O, **1-Er**·35H₂O and **2-Er**, respectively, are all consistent with the values of 35.4 (Tb, ⁷F₆), 42.5 (Dy, ⁶H_{15/2}), 42.2 (Ho, ⁴I₈) and 34.4 (Er, ⁴I_{15/2}) cm³ mol⁻¹ K expected for three-non-interacting lanthanoid(III) centers. The decrease in $\chi_M T$ observed as the temperature is decreased below 100 K is due to the effect of CF splitting and possibly a contribution from intramolecular exchange interactions between the three lanthanoid(III) centers. Unfortunately, a spin-only Gd analog is not available to probe this aspect. For reference, $J_{\text{Gd}...\text{Gd}}$ coupling constants of -0.04 cm⁻¹ ($\hat{H} = -\sum J_{ij} \hat{S}_i \cdot \hat{S}_j$) and -0.004 cm⁻¹ ($\hat{H} = -2\sum J_{ij} \hat{S}_i \cdot \hat{S}_j$) have been reported for gadolinium(III) complexes bridged by $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-carbonate}$ ligands.⁵⁵ The low temperature values of the $\chi_M T$ plots are indicative of the ground state of the ions. For both **1-Tb** and **1-Ho**, $\chi_M T$ appears to approach a 0 cm³ mol⁻¹ K at low temperature, suggesting a CF ground state dominated by low M_J values. The low temperature values of around 30 and 21 cm³ mol⁻¹ K for **1-Dy** and **1-Er**, respectively, indicate magnetic ground states, as expected

for an odd number of Kramers ions. Comparison of the data for **1-Er**·35H₂O and **2-Er** reveals minor differences in the magnetic susceptibility profile. The low temperature $\chi_M T$ data approach a similar value for both **1-Er**·35H₂O and **2-Er** suggesting similar ground states for both compounds. The low temperature magnetization plots are typical for lanthanoid(III) **mononuclear** complexes and do not exhibit the sigmoidal shape observed previously for triangular dysprosium(III) complexes found to exhibit a toroidal magnetic moment.^{36, 38}

Figure 2. Magnetic susceptibility data for **1-Ln**·35H₂O for Ln = Tb (■), Dy (●), Ho (▲) and Er (▼) and **2-Er** (◄), measured with an applied field of 1 kOe from 2-70 K and 10 kOe from 70-300 K. Inset with temperature range from 0-45 K to show low temperature trend.

The dynamic magnetic behavior of **1-Ln**·35H₂O (Ln = Tb, Dy, Ho and Er) and **2-Er** was investigated by use of alternating current (ac) susceptibility measurements with ac frequencies in the range 50-1500 Hz. These measurements were performed both without an applied dc field and with an applied dc field of 2 kOe (Figures 3, 4, S8-S11). This value of the applied dc field was selected based on a scan of field-dependence at several temperatures in the range 2-4 K. None of the compounds exhibit frequency-dependent behavior or peaks in the out-of-phase susceptibility in the absence of an applied dc field. However, the application of a 2 kOe dc field, to suppress quantum tunneling of the magnetization, affords

frequency-dependence, with an increase in χ_M'' and concomitant decrease in χ_M' observed for **1-Dy**·35H₂O, **1-Er**·35H₂O and **2-Er**. No peak maxima are evident in the measured temperature and frequency range, except for **1-Dy**·35H₂O at the highest frequency of 1500 Hz. Data were also acquired as a function of frequency for **1-Dy**·35H₂O, **1-Er**·35H₂O (Figure S11) and again no clear set of peaks are evident. The absence of peaks in out-phase-susceptibility does not allow the extraction of an energy barrier for these weak field-induced SMMs, assuming an energy activated process that follows an Arrhenius law.

Figure 3. In-phase and out-of-phase ac magnetic susceptibility for **1-Dy·35H₂O** measured without an applied dc field (top) and with an applied field of **2 kOe** (bottom). The ac frequencies are given in the legend.

Figure 4. In-phase and out-of-phase ac magnetic susceptibility for **1-Er**·35H₂O measured without an applied dc field (top) and with an applied field of 2 kOe (bottom). The ac frequencies are given in the legend.

Inelastic Neutron Scattering. Inelastic neutron scattering data were collected for the deuterated **1-Ho^D** and **1-Er^D** analogs to probe the CF splitting of the respective $J = 8$ and $15/2$ ground states. Although magnetically interesting it was decided not to measure the INS spectrum of **1-Dy**. This is due to the high absorption cross-section of Dy with cold neutrons thus precluding measurement with a neutron wavelength of 4.75 Å. Although it is possible to measure a thermal spectrum on PELICAN utilizing 2.375 Å wavelength neutrons, there is a

significant flux penalty in doing so. Given this fact, coupled to the high absorption even with thermal neutrons (approx. 900 barn), it was decided that this was not a feasible experiment. Previous work has successfully measured a signal for a Dy complex,¹² however this experiment utilized a thermal neutron instrument. The INS data were compiled and analyzed using Gaussian least square fitting paired through LAMP with a detailed balance term, $S(Q, -\omega) = S(Q, \omega)e^{\frac{-\hbar\omega}{k_B T}}$. The detailed balance accounts for transitions observed both on the energy loss and gain side of the spectrum. The peaks observed were then assigned as ground or excited state transitions through analysis of data from various temperatures. As the molecule contains three distinct lanthanoid(III) environments, the assignment of peak locations is representative of a convolution of three separate transitions. Therefore, the fitted peak locations correspond to a combined contribution from the individual sites.

Spectra were also acquired for the diamagnetic **1-Y^D** analog to determine the phonon background. Analysis of the data measured for **1-Y^D** with neutron wavelengths $\lambda = 4.74$ and $2.37 \text{ \AA}$ reveals a peak at 3 meV (Figure S12). This was observed at both 5 and 50 K and the intensity increased with increasing momentum transfer vector (Q), indicative of a phonon transition. This phonon background was compared with the spectra obtained for the **1-Ho^D** and **1-Er^D** analogs to illustrate the existence of magnetic signals (Figure S13).

The spectra collected for **1-Ho^D** at neutron wavelengths $\lambda = 4.74$ and $2.37 \text{ \AA}$ are presented in Figure 5. Clear peaks in the spectra are evident at ~ 0.5 meV and ~ 3 meV. The analysis of the temperature and Q dependence (Figures S14 and 15) suggests these are magnetic excitations. The two well-resolved, but broad peaks, with fit peak maximum positions of 0.608(1) (**I**) and 3.05(1) (**II**) meV, are observed on both the neutron energy loss (**I** and **II**) and gain (**I'** and **II'**) sides of the spectrum.

Figure 5. Variable temperature INS spectra of **1-Ho^D** at $\lambda = 4.74$ Å (left) and 2.37 Å (right), summed over all scattering angles, spectra offset for each temperature. Positive numbers correspond to neutron energy loss. Magnetic transitions are labelled with Roman numerals as described in the text.

An initial observation of the peaks is that they are significantly broader than the resolution of the instrument, with **I** exhibiting a full width at half maximum (FWHM) of $0.993(3)$ meV and **II** a width of $\sim 1.98(4)$ meV. There are two possible causes of the peak broadening; firstly the sample is comprised of three crystallographically inequivalent Ho(III) ions, the broadness of the peaks can be mainly attributed to small differences in the Ho(III) coordination environments affording three overlapping magnetic transitions contributing to each peak. Secondly, the width of the peak is directly related to the lifetime of the excitation, with broad excitations implying a short lifetime. Peak broadening of CF excitations has been observed previously and can be due to effects such as vibrational dampening of the excitations or energy dissipation via conduction electrons.^{61, 62} As **1-Ho^D** is an insulator, the latter is not possible, while the former would result in a temperature dependence of the peak width, with the peaks anticipated to become resolution limited at 5 K when the phonon amplitudes are small. The peak broadening in these cases typically gives rise to a Lorentzian

lineshape convoluted with the instrument resolution. In the case of **1-Ho^D**, a regular Gaussian lineshape is observed; a similar effect has been observed in the CF spectrum of Tb₂Ti₂O₇ a highly frustrated magnet from the pyrochlore oxide family that shows a spin liquid ground state.^{63, 64} This has been postulated to be due to a random field from surrounding fluctuating moments.

While the peak positions of the observed transitions were assigned through the fitting with a single Gaussian curve (Figure S16), a fitting using three peaks was also investigated to account for the three discrete Ho(III) environments (Figure S17). Invoking multiple peak fits also requires each of the peak widths to be significantly greater than the instrument resolution, with FWHM ranging between 0.45 and 0.9 meV. Multiple peak fitting enables a more accurate description of the temperature dependence observed in the peaks. If multiple transitions are present, then it is expected that upon heating, the relaxation processes would increase differently, resulting in asymmetric peaks.

The temperature dependence of the INS peaks indicates that these are magnetic excitations from the CF ground state and upon increasing the temperature to 10, 20 and 50 K, the intensity of these "cold" transitions decreases and no new peaks are observed. The resulting CF splitting diagram then places the relative energies of the three lowest energy CF states (**0-2**) at 0, 0.6 and 3 meV (Figure 6, left). There is no evidence of "hot" transitions from excited states **1** or **2** to higher energy CF states in the spectra obtained; however, it is possible that these are masked beneath the broad peaks of the ground state transitions. The 3 meV peak (**II'**) on the neutron energy gain side of the $\lambda = 4.74$ Å spectrum is only well resolved at 50 K when there is significant thermal population of CF state **2**.

Figure 6. Energy level diagrams and INS transitions for 1-Ho^D (left) and 1-Er^D (right) derived from INS data. Transition III for 1-Er^D is either $1 \rightarrow 3$ or $2 \rightarrow 3$.

The spectra of 1-Er^D (Figure 7) collected with 4.74 Å wavelength neutrons show only the beginning of a broad peak (I) at the spectral limit with no peak maximum evident. No transitions are evident on the neutron energy gain side of the spectrum at 5 K, although the 50 and 80 K spectra reveal three bands. The lowest lying transition with a peak position around 2.5 meV (I') is well resolved at both of these temperatures. There is also evidence of broad features around 5 (II') and 9 (III') meV, both most prominent in the 80 K spectrum. The base temperature spectrum (4.7 K) collected using 2.37 Å neutrons shows one well resolved transition around 2.5 meV (I) and a broad feature with a peak maximum around 5 meV (II). Attempts to fit the data for 1-Er in the same manner as for 1-Ho were not as successful due to the weak intensity and broad, overlapping nature of the peaks. As a result, we report here the positions of the peak maxima for the observed peaks. The temperature and Q dependence (Figure S18) are again consistent with the assignment of these transitions as magnetic. As the intensity of transition I decreases with increasing temperature, this is assigned as a transition between the two lowest lying CF split microstates of the $J = 15/2$ ground state of the Er(III) ions, labelled as 0 and 1 (Figure 6, right). Transition II is most likely the ground state

transition $0 \rightarrow 2$, as it is evident in the low temperature data; however, the intensity of this peak shows very little temperature dependence. Analysis of the temperature dependence of spectra collected at higher temperatures suggests the presence of a band associated with a transition between excited states, which is clearly resolved in both the 50 and 80 K spectra at an energy of around 9 meV (**III**). This compares well with the feature observed on the neutron energy gain side of the $\lambda = 4.74 \text{ \AA}$ spectrum. Peak **III** is not evident in the base temperature spectra and is difficult to assign as it shows very little temperature dependence. It can be assigned as an excited state to excited state "hot" transition; but it is not possible to distinguish between the two possibilities: $1 \rightarrow 3$ or $2 \rightarrow 3$ (Figure 6) on the basis of the INS data alone. Based on the observed transitions, the third excited state (**3**) is thus determined to be either 12 or 14 meV above the ground state.

Figure 7. Variable temperature INS spectra of 1-Er^{D} at $\lambda = 4.74 \text{ \AA}$ (left) and $2.37 \text{ \AA}$ (right), summed over all scattering angles, spectra offset for each temperature. Positive numbers correspond to neutron energy loss. Magnetic transitions are labelled with Roman numerals as described in the text.

Ab Initio Calculations. To complement the INS and magnetic studies, *ab initio* calculations were performed, using as input structural data obtained from single crystal X-ray diffraction studies of **1-Ho**·42H₂O and **1-Er**·42H₂O at 130 K. The separate calculations carried out on the crystallographically distinct lanthanoid(III) sites establish a clear difference in the energy splitting resulting from the slight variations in the coordination environment. As a consequence, all the theoretically calculated quantities for the three different Ho(III) or Er(III) positions were summed when compared with the experimental data. The thermal dependence of magnetic susceptibility over the temperature range 0 to 300 K and field dependence of the magnetization from 0 to 50 kOe (Figures 8 and 9) were computed using the Single Aniso module of Molcas.

Figure 8. Comparison of experimental data for **1-Ho**·35H₂O (red) and *ab initio* calculated curves for **1-Ho**·42H₂O (black): variable temperature magnetic susceptibility (main) and magnetization data at 2 K (inset).

Figure 9. Comparison of experimental data for **1-Er·35H₂O** (red) and *ab initio* calculated curves for **1-Er·42H₂O** (black): variable temperature magnetic susceptibility (main) and magnetization data at 2 K (inset).

The energy spectra resulting from the calculation across the three structurally inequivalent Ho(III) sites for **1-Ho·42H₂O** exhibit deviation across the sites (Table S2). The lowest lying CF states are presented in Table 3 and are singlet states for the non-Kramers Ho(III) ion. The calculated magnetic susceptibility curve (Figure 8) is in excellent agreement with the experimental data, with a slight deviation approaching room temperature. The low temperature value of $\chi_M T$ approaches 0 cm³ mol⁻¹ K at 0 K, which is consistent with the experimental data and the absence of SMM behavior. The calculated magnetization curve is also in excellent agreement with the experimental data (Figure 8).

Table 3. Energies (meV) for the five lowest energy CF states calculated *ab initio* for the three Ho(III) sites in **1-Ho·42H₂O**.

State	Ho1	Ho2	Ho3	Average
0	0	0	0	0

1	1.8	1.5	0.64	1.3
2	1.9	2.2	4.9	3.0
3	4.3	4.2	6.1	4.9
4	20.4	19.5	21.8	20.6

Decomposition of the wavefunctions is difficult for **1-Ho**·42H₂O, as the ground state is not a pure doublet. As a result, the magnetic axis determined from the four singlet states lying at lowest energy was employed for this purpose. Decomposing the wavefunctions with respect to this axis gives a consistent assignment across the different Ho sites. The modulus square values of the *ab initio* matrix elements of the magnetic moment operator between ground and the three excited states are 7.96 (**0** → **1**) 6.19 (**0** → **2**) and 6.91×10^{-2} (**0** → **3**), showing that while transitions **0** → **1** and **0** → **2** are expected to be INS-active, transition **0** → **3** is predicted to be silent, consistently with the experimental observations

Analogous calculations were performed for the three Er sites of **1-Er**·42H₂O to determine the variation across the three Er(III) sites. The overall profiles of the energy spectra are similar for the different Er(III) centers, with less deviation observed across the three sites (Table 4). Magnetic susceptibility curves were calculated for the three Er(III) sites and summed to give the overall molecular response, which is in reasonable agreement with the experimental data (Figure 9). The magnetization curve calculated for the sum of the three independent sites (Figure 9) is in good agreement with the low field experimental data and the low temperature slope is an excellent match, with this gradient representative of the CF ground state. The divergence at high field of the magnetization curve predicted *ab initio* from the experimental data is consistent with the difference between the energy spectrum predicted *ab initio* and that derived from observed INS transitions. This arises from the occupancy of low-lying excited states, which contribute to the measured magnetization values at higher fields.

Table 4. Energies (meV) for the five lowest energy CF levels calculated *ab initio* for the three Er(III) sites in **1-Er**·42H₂O.

State	Er1	Er2	Er3	Average
0	0	0	0	0
1	7.3	5.8	7.2	6.8
2	12.7	11.1	12.3	12.0
3	22.3	20.9	22.7	22.0
4	25.7	24.3	26.0	25.3

The CF ground state (**0**) for **1-Er**·42H₂O can be described by the calculated wavefunctions based on the projection of the ground doublet state (Table S4). When computing the wavefunctions in this way, the ground term across the three sites is found consistently to be a dominant mixture of the $|\pm 15/2\rangle$ and $|\pm 11/2\rangle$ with some slight variation in the proportion. Both, Er1 and Er3 have very similar compositions with $0.69|\pm 15/2\rangle$ and $0.24|\pm 11/2\rangle$, and $0.68|\pm 15/2\rangle$ and $0.27|\pm 11/2\rangle$, respectively. Center Er2 shows a slightly lower contribution of $|\pm 15/2\rangle$. The decomposition calculated for Er2 had major contributions of $0.58|\pm 15/2\rangle$ and $0.34|\pm 11/2\rangle$.

The $T = 0$ intercepts of the *ab initio* $\chi_M T$ curves for each Er(III) ion, which in cm³ K mol⁻¹ correspond to $0.12505 (g_{xx}^2 + g_{yy}^2 + g_{zz}^2)/4$ with g_{xx} , g_{yy} and g_{zz} the *ab initio* principal components of the ground KD g -tensor (Tables S3 and S4), are found to be $(\chi_M T)_{T=0} = 8.3$ cm³ K mol⁻¹ for Er1, $(\chi_M T)_{T=0} = 7.6$ cm³ K mol⁻¹ for Er2, and $(\chi_M T)_{T=0} = 8.2$ cm³ K mol⁻¹ for Er3. If the three centers are magnetically uncoupled, the *ab initio* $\chi_M T$ for the molecular ring is simply evaluated as the sum of $\chi_M T$ for the three independent centers, leading to $(\chi_M T)_{T=0} = 24$ cm³ K mol⁻¹ (intercept of the solid black line in Figure 9). Note that

at 2 K the *ab initio* curve shows a very small deviation from the zero- T intercept (due to temperature independent paramagnetism), with $(\chi_M T)_{T=2\text{K}} = 24.5 \text{ cm}^3 \text{ K mol}^{-1}$. Given that the lowest temperature experimental value for $\chi_M T$ ($T = 2 \text{ K}$) is $21 \text{ cm}^3 \text{ K mol}^{-1}$, and that the overall comparison between the *ab initio* and experimental curves reported in Figure 9 is good, we conclude that intramolecular Er...Er magnetic coupling is negligible in **1-Er** (i.e. much smaller than the 2K base temperature explored here), consistent with literature Gd analogs.⁵⁵ In this magnetically uncoupled picture, since each Er center contributes a doublet, the ground state for the Er-triangle consists of $2^3 = 8$ degenerate states, in which the relative orientation of the magnetic moments on any pair of Er ions is equally probable. This also means that we do not expect the ground state to be described by a non-collinear collective magnetic configuration, such as a non-magnetic KD corresponding to a toroidal moment, as found in some other Ln-triangles.³⁶⁻³⁸

However, dipolar interactions are non-negligible in polynuclear lanthanoid complexes where the ions have a large ground state magnetic moment. In this case the average magnetic moment per Er(III) ion is $m \sim 8\beta$, given the mixed $|\pm 15/2\rangle$ (~70%) and $|\pm 11/2\rangle$ (~30%) character of the ground KD wavefunctions, so that one would expect to observe the fingerprint of such interactions at low temperature. We argue here that the experimental evidence for negligible magnetic coupling can be explained in terms of antiferromagnetic superexchange interactions between the Er(III) ions, which must be as strong as dipolar interactions, but of opposite sign.

In fact our *ab initio* calculations suggest that the ground state g -tensor of each Er(III) ion is almost purely axial, with the principal magnetic axis nearly co-planar with the triangular ring (the angles of the magnetic axes with the normal to the triangular plane are 80.3° for Er₁, 97.0° for Er₂, and 98.1° for Er₃), and directed almost exactly along the local *radial* direction for each Er(III) ion, connecting the centroid of the triangle with the Er(III)

ion (the angles of the magnetic axes with the corresponding exact in-plane radial directions are 9.8° for Er1, 7.6° for Er2, and 8.2° for Er3; Figure 10). The principal magnetic axis for each Er(III) ion is nearly coincident with the bond to the single terminal aqua ligand of the seven-coordinate erbium centers. This alignment likely stabilizes the prolate charge distribution of the Er(III) ion,⁸ given that the oxygen donor atom of the aqua ligand is the only uncharged donor atom in the coordination sphere of each Er(III) and the Er-O(H₂) bond is relatively long.

Figure 10. Schematic representation of the direction of the three principal magnetic axes for Er1 (red arrow), Er2 (blue arrow) and Er3 (green arrow) ions in **1-Er**, showing their nearly exact co-planarity with the triangular ring (left), and their nearly exact radial orientation (right). Exact in-plane radial (thin black arrows) and tangential (thin gray arrows) directions are also indicated to illustrate the deviation of the magnetic axes from perfect radial orientation.

An estimate of the dipolar interactions can thus be made by assuming an equilateral triangle geometry, with sides corresponding to the average experimental Er...Er distance $d \sim 4.8 \text{ \AA}$, and assuming the local Er(III) magnetic anisotropy is purely axial, oriented exactly along the radial direction, with the calculated average magnetic moment $m \sim 8\beta$. With such

approximations, it can be shown that the 8-fold degeneracy of the ground state of the non-interacting triangular ring would be split by dipolar interactions into a 6-fold degenerate ground state with a magnetic moment $M_0 = 2m = 16\beta$ and dipolar energy $-7m^2/4d^3$, separated from an excited *non-magnetic* KD ($\mathbf{M} = \sum_{i=1}^3 \mathbf{m}_i \sim 0$) with dipolar energy $+21m^2/4d^3$ and a large *radial magnetic moment* that we define as $\rho = \sum_{i=1}^3 \mathbf{r}_i \cdot \mathbf{m}_i \sim \pm (24/\sqrt{3}) d \beta$ (where $\mathbf{r}_i$ is the position of the i^{th} Er-center), resulting in an energy gap $\Delta_{\text{dip}} = 7m^2/d^3 \sim 1.8 \text{ cm}^{-1} = 2.6 \text{ K} = 0.22 \text{ meV}$ (Figure 11).

Figure 11. Expected energy splitting of the 8-fold degenerate ground state (left) of the non-interacting Er-triangle in **1-Er**, based on Er...Er dipolar magnetic coupling (H_{dip}) stabilizing a non-collinear "ferromagnetic" 6-fold degenerate ground state with magnetic moment $M_0 = 16\beta$ (middle), and observed non-split ground state (right), arguably due to the existence of competing antiferromagnetic exchange coupling interactions (H_{exch}) of similar magnitude to

the dipolar coupling, stabilizing the Kramers doublet with a *radial magnetic moment* $\rho = \sum_{i=1}^3 \mathbf{r}_i \cdot \mathbf{m}_i \sim \pm (24/\sqrt{3}) d \beta$ and a *zero dipolar magnetic moment* $\mathbf{M} = \sum_{i=1}^3 \mathbf{m}_i \sim 0$.

If only dipolar interactions were at work, one would expect $(\chi_M T)_{T=0} = 0.12505 M_0^2 \sim 32 \text{ cm}^3 \text{ K mol}^{-1}$, a much larger value than the calculated $(\chi_M T)_{T=0} \sim 24 \text{ cm}^3 \text{ K mol}^{-1}$ based on the uncoupled ions approximation, which, in turn, compares well with $(\chi_M T)_{T=2 \text{ K}} \sim 21 \text{ cm}^3 \text{ K mol}^{-1}$ observed experimentally at 2 K. Even accounting for a reduction factor of the low temperature $\chi_M T$ due to the thermal population of the first non-magnetic (radial) excited doublet at $T = 2 \text{ K}$, the dipolar-coupled system would still feature a $(\chi_M T)_{T=2 \text{ K}} \sim 29 \text{ cm}^3 \text{ K mol}^{-1}$, still too large to account for the experimental observations.

Hence, the experimental evidence for non-interacting Er ions suggests the existence of competing *antiferromagnetic* exchange interactions, which can be modeled by assuming that the interaction consists of an isotropic Heisenberg exchange Hamiltonian $H_{\text{exch}} = -J_{\text{exch}}(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_3 \cdot \mathbf{S}_1)$ describing an antiferromagnetic interaction ($J_{\text{exch}} < 0$) between the true spin moments ($\mathbf{S}_i$) of the Er(III) ions,^{36, 65} hence, stabilizing the non-magnetic KD carrying radial magnetic moment ρ , and cancelling the effect of dipolar coupling. To make a rough estimation of the value of J_{exch} , we assume for simplicity that the wavefunction over the three Er centers is the same and consists of 70% of $|\pm 15/2\rangle$ and 30% of $|\pm 11/2\rangle$, and thus the matrix element of the Er_i spin component along the quantization axis, evaluated on the ground doublet $|\pm \Psi_i\rangle$, is approximated to $\langle \pm \Psi_i | S_{Z,i} | \pm \Psi_i \rangle \sim 0.7 (\pm 3/2) + 0.3 (\pm 11/10) = \pm 1.38$. Within the 8-fold degenerate ground manifold found by *ab initio* calculations, H_{exch} is in fact projected on a non-collinear Ising Hamiltonian featuring the interaction between neighboring $S_{Z,i}$ spin-operators with each $S_{Z,i}$ quantized along its own radial magnetic axis.⁶⁸ Such a Hamiltonian is clearly diagonal, so that the exchange gap Δ_{exch}

can be easily calculated as the energy of the radial doublet ($E_{\text{exch}} = 3 (1.38)^2 J_{\text{exch}} / 2$) minus that of the magnetic sextet ($E_{\text{exch}} = -(1.38)^2 J_{\text{exch}} / 2$), leading to $\Delta_{\text{exch}} = 2 (1.38)^2 J_{\text{exch}}$, which as anticipated, if $J_{\text{exch}} < 0$, favours the (non-magnetic) radial doublet as the ground state. In order for the dipolar and superexchange mechanisms to exactly cancel out each other, we need to have $\Delta_{\text{exch}} = -\Delta_{\text{dip}}$, from which we obtain $J_{\text{exch}} = -0.47 \text{ cm}^{-1}$ (-0.058 meV). The cancellation between dipolar and superexchange interactions does not have to be exact, but measurements of χ_{MT} below 2 K would be necessary to determine the actual magnitude of a possible residual gap, and establish whether the ground state becomes magnetic or non-magnetic for $T \rightarrow 0$.

Implications of *Ab Initio* Results for Magnetic Behavior and INS Spectra. It is important to bear in mind that the *ab initio* calculations are based on structural data obtained at only a single temperature point for fully hydrated samples, whereas the magnetic and INS data are collected at a range of temperatures down to 2 K and are measured on partially dehydrated samples. Nevertheless, the agreement of the measured and calculated magnetic susceptibility and magnetization profiles for **1-Er** and **1-Ho** is very good.

A comparison of the lowest lying CF split energy levels (**0** to **3**) calculated *ab initio* and inferred from INS spectral data for **1-Ho** are singlets with the excited states lying within 5 meV of the ground state (Figure 12). The calculated energy of the **0** $\rightarrow$ **1** transition of 1.3 meV is in reasonable agreement with the broad peak observed in the INS spectrum at 0.6 meV (**I**). The second excited state (**2**) is calculated around 3 meV, which is in excellent agreement with the energy derived from the INS spectrum from the **0** $\rightarrow$ **2** transition (**II**). A third CF excited state is also predicted at 4.8 meV (labelled **3**), however, *ab initio* calculations indicate that the matrix elements of the total angular momentum operator

between the ground state and this excited state is zero, hence the transition is INS-silent. The remaining CF excited states are determined to be above 19 meV and transitions involving these would therefore not be observed by INS. Some "hot" excited-excited state transitions are also predicted, however these exist within the range of the observed "cold" transitions from the CF ground state and could be masked beneath the broad peaks. The prediction of a singlet ground state and low lying excited states supports the lack of SMM behavior observed for **1-Ho**.

Figure 12. Energy level diagrams derived *ab initio* and from INS data for **1-Ho^D** (left) and **1-Er^D** (right).

Energies calculated for **1-Er** do not show the same level of agreement with experiment as those for **1-Ho** (Figure 12). The first excited CF state (**1**) is calculated at an average relative energy of 6.8 meV. The second (**2**) and third (**3**) excited states are calculated to lie beyond the available INS energy range, with energies around 12 meV and 22 meV, respectively. The INS measurements reveal two cold transitions and a single hot transition within the accessible energy range. The calculated energies of the first four states are all higher than the INS spectra would suggest.

While the *ab initio* energies are not in ideal agreement with the measured ones, the calculated matrix elements are helpful in assigning the INS transitions. Non-zero matrix

elements between states **0** and **1**, and **0** and **2**, are predicted from *ab initio* calculation, which is consistent with the observation of transitions **I** and **II** between these levels in the INS spectra. There is also a non-zero matrix element between states **0** and **3**, however, the observation of the hot transition (**III**) in the INS spectra places **3** beyond the limit of the INS range and the **0** $\rightarrow$ **3** transition would not be observed in the spectra collected with a neutron wavelength of 2.37 Å. The calculations suggest that transitions **1** $\rightarrow$ **3** and **2** $\rightarrow$ **3** are both allowed, with non-zero matrix elements between the states involved in both cases and in principle, the only observed hot transition (**III**) up to 10 meV could correspond to either of these transitions. However, the assignment of transition **III** as a **1** $\rightarrow$ **3** transition would require the existence of another hot transition (**2** $\rightarrow$ **3**) at around 7 meV which is predicted to have a larger intensity than the 9 meV peak (Figure S19). As this transition is not observed, transition **III** is instead assigned as a **2** $\rightarrow$ **3** transition and the energy of level **3** is inferred to be 14 rather than 12 meV (Figure 12).

Also consistent with INS and magnetic measurements, is the *ab initio* calculation of mixed high M_J contributions to the composition of the ground state doublet for **1-Er**. The high M_J component shows the potential for SMM behavior; however, the weak out-of-phase ac susceptibility signal is consistent with the low lying excited states observed and heavy mixing of these states. This indicates that significant mixing of the wavefunctions, as suggested by *ab initio* calculations, enhances the quantum tunneling observed and provides alternate relaxation pathways other than an Orbach process relaxation through the first excited state. Unfortunately, the resolution of the current INS spectra and the broadness of the observed INS peaks prohibit drawing any conclusions about the predicted Er...Er coupling.

Concluding Remarks

In this work, a systematic synthetic effort has provided access to an isomorphous family of $\text{Na}_{11}[\{\text{RE}(\text{OH}_2)\}_3\text{CO}_3(\text{PW}_9\text{O}_{34})_2]$, allowing a comprehensive study of the magnetic properties and electronic structures of the different analogs. Alternating current magnetic susceptibility measurements indicate that the analogs incorporating the Kramers ions Dy(III) and Er(III) are field-induced SMMs, while the non-Kramers Tb(III) and Ho(III) analogs are not SMMs. Inelastic neutron scattering studies of the Er(III) and Ho(III) compounds have allowed accurate mapping of the energies of the lowest lying CF split energy levels of the respective $J = 8$ and $15/2$ ground states of the three structurally inequivalent lanthanoid(III) ions in each compound. Complementary *ab initio* calculations performed on these two analogs provide insight into the observed magnetic behavior, indicating significant mixing of the M_J contributions to the CF split energy levels. For the Er(III)-containing SMM, high magnitude M_J are the dominant contributors to the ground state, while low magnitude M_J values are the major contributors to the ground state of the non-SMM Ho(III) complex. The *ab initio* calculated magnetic susceptibility and magnetization curves are in excellent agreement with experimental data, and the *ab initio* determined energies of the lowest lying CF split levels are in good agreement of the values inferred from INS data. Importantly, the *ab initio* determined matrix elements of the magnetic moments between the states are consistent with the observed presence or absence of CF transitions in the INS spectra and in some cases are invaluable in assigning the INS transitions.

In each complex, the three structurally inequivalent lanthanoid(III) ions are linked by a $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -carbonate bridging ligand, with intramolecular Ln $\cdots$ Ln separations of approximately 4.8 Å. Although superexchange between lanthanoid(III) ions is generally weak, it is pertinent to consider it given the short internuclear distances. Indeed, there is no

evidence in either magnetic or INS data for any $\text{Ln}\cdots\text{Ln}$ coupling. The *ab initio* calculations performed on three distinct ions and summed to model the trinuclear lanthanoid complexes give excellent agreement with the measured magnetic data. The INS spectra were modeled as three equivalent ions, although the observed broadness of the peaks may well be due to the existence of three slightly different coordination environments. Interestingly, *ab initio* calculations on the Er(III) analog indicate that the ground state g -tensor of each Er(III) ion is almost purely axial, with the principle magnetic axes nearly coplanar with the plane of the Er-triangle and oriented almost exactly along the local radial direction for each Er. While antiferromagnetic isotropic exchange interactions *and* the radial arrangement of the magnetic axes would stabilize a large radial magnetic moment in the trinuclear Er complex, we showed here that dipolar interactions tend to destabilize this radial configuration in favour of a non-collinear ferromagnetic arrangement in the ground state. Since INS and magnetic data show overall negligible magnetic coupling, we conclude that non-negligible carbonate-mediated superexchange interactions exist in this complex, which must be of similar magnitude and opposite sign (i.e antiferromagnetic) to competing intramolecular dipolar $\text{Er(III)}\cdots\text{Er(III)}$ interactions.

We conclude by noting that isotropic antiferromagnetic superexchange interactions in a Ln-triangle with either all radial or all tangential orientations of the easy-axes, will always stabilize the non-collinear moment configuration with a zero magnetic moment for the ground state. This is irrespective of whether it is a radial moment as in the Er analog studied herein, or a toroidal moment as observed in other cases, and thus isotropic superexchange does not allow distinction between radial or toroidal configurations. On the other hand, the anisotropic character of the magnetic dipolar interactions can in fact allow distinction between radial and tangential (toroidal) non-collinear arrangement of the axes in a triangle: while with radial magnetic axes, as seen here, dipolar interactions will *compete* with

antiferromagnetic exchange resulting in overall negligible intramolecular magnetic coupling. For a toroidal arrangement of the magnetic axes, dipolar interactions will always *cooperate* with antiferromagnetic exchange interactions to stabilize a toroidal moment in the ground state. These findings would appear to suggest that toroidal magnetic moments should be more easily detectable than radial magnetic moments in Ln-triangles, at least down to the usually explored base temperatures of 2 K. In fact, if a triangular lanthanoid(III) complex has tangential anisotropy axes, dipolar interactions alone would suffice to stabilize a toroidal "non-magnetic" Kramers doublet, even if antiferromagnetic superexchange is negligible.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic files in CIF format for **1-RE**·42H₂O (RE = Y, Tb, Dy, Ho, Er), additional structural, TGA, IR, magnetic INS and *ab initio* data; this material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors

* c.boskovic@unimelb.edu.au and asoncini@unimelb.edu.au

Author Contributions

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Table of Contents Graphic and Synopsis

Alternating current magnetic susceptibility studies of $\text{Na}_{11}[\{\text{RE}(\text{OH}_2)\}_3\text{CO}_3(\text{PW}_9\text{O}_{34})_2]$ (**1-RE**) indicate **1-Dy** and **1-Er** are field-induced single-molecule magnets, while inelastic neutron scattering spectra and *ab initio* calculations for **1-Ho** and **1-Er** provide insights into the crystal field splitting that gives rise to the observed magnetic behavior.