Unparalleled selectivity and electronic structure of heterometallic [LnLn'Ln] molecules as 3-qubit quantum gates

Diamantoula Maniaki, Diego Garay-Ruiz, Leoní A. Barrios, Daniel O. T. A. Martins, David Aguilà, Floriana Tuna, Daniel Reta, Olivier Roubeau, Carles Bo and Guillem Aromí

Supplementary Information

<u>Synthesis</u>

Ligand H₂LA was prepared according to our published procedure.¹ Ligand H₂LB was prepared as previously reported by our group.²

[PrEr₂(LA)₂(LB)₂(py)(H₂O)₂](NO₃) (1)

A light brown solution of H₂LA (10.2 mg, 0.032 mmol) and H₂LB (14.8 mg, 0.032 mmol) in pyridine (10 mL) was added dropwise under stirring to a colorless solution of Pr(NO₃)₃·6H₂O (7 mg, 0.016 mmol), Er(NO₃)₃·5H₂O (14.2 mg, 0.032 mmol) and CuCl₂·2H₂O (2.7 mg, 0.016 mmol) in pyridine (10 mL). The resulting green solution was left under stirring for 1 h and layered with hexane. After a week, green crystals of [Cu(py)₄(NO₃)₂] were obtained. After one month, large orange crystals of **1** were easily separated from the rest. Yield: ~15%. Elemental analysis (C,H,N): calcd (found) for 1·4H₂O: C, 54.88 (54.64); H 3.38, (2.96); N. 3.66 (3.71). Metal analysis (mols Pr/mols Er, IPC): calc 0.50 (0.53). MS: m/z = 2049.1867 [PrEr₂(LA)₂(LB)₂]⁺, 1024.5845 ([Er₂Pr(LA)₂(LB)₂]+H⁺)²⁺, 1035.5858 ([Er₂Pr(LA)₂(LB)₂]+Na⁺)²⁺.

IR: $\tilde{v} = 3051 \text{ (mb)}$, 1627 (s), 1581 (s), 1560 (s), 1517 (s), 1445 (s), 1399 (m), 1384 (s), 1284 (m), 1196 (m), 1125 (m), 1063 (w), 956 (m), 781 (m), 757 (w), 691 (w), 660 (w), 521 (w).

Elemental Analysis

C, H, N analyses were performed by using a Thermo EA Flash 2000 (Thermo Scientific) analyser at the Centres Científics i Tecnològics from the Universitat de Barcelona (CCiT-UB). Metal analysis was performed through Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) at the Mikroanalytisches Labor Pascher Laboratory.

Magneto-thermal characterization

Magnetic measurements were performed with a commercial MPMS-XL SQUID magnetometer at the Physical Measurements Unit of the Servicio General de Apoyo a la Investigación-SAI, Universidad de Zaragoza. The data were corrected for the

contribution of the capsule sample holder, determined empirically. The sample diamagnetic contributions to the susceptibility were corrected using Pascal's constant tables. Direct current (dc) data were collected at variable temperature between 2 and 300 K with an applied field of 1000 Oe, as well as at 2 K at variable fields up to 5 T.

Heat capacities in the range of 0.35–30 K were obtained using the relaxation method in a commercial ³He set-up equipped with a 9 T magnet, at the same facility. Apiezon-N grease was used to provide good internal thermal contact between the heater, thermometer and sample. The sample was in the form of a thin pellet.

Single Crystal X-ray Diffraction (SCXRD)

Data for compound **1** were acquired on a 30x30x20 mm yellow block at 100 K on the XALOC-BL13 beamline of the ALBA synchrotron ($\lambda = 0.72932$ Å).³ Data reduction and absorption corrections were performed through XIA2, which uses CCP4 DISTL, LABELIT, POINTLESS and XDS softwares.⁴ The structure was solved by intrinsic phasing with SHELXT⁵ and refined by full-matrix least-squares on F^2 with SHELXL.⁶ A void containing only diffuse electron density was analyzed and taken into account with PLATON/SQUEEZE,⁷ giving an estimated content of two diffuse lattice pyridine molecules per cell that were included in the formula. All details can be found in CCDC-2142740 that contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via https://summary.ccdc.cam.ac.uk/structure-summary-form. Crystallographic and refinement parameters are summarized in Table S1. Intramolecular metal...metal separations and metal-donor bond lengths describing the coordination environments of the metal sites are given in Table S2. Hydrogen bond details are given in Tables S3.

Table S1. Crystallographic and refinement parameters for the structure of compound $[PrEr_2(LA)_2(LB)_2(py)(H_2O)_2](NO_3)\cdot 10py$ (1).

Compound	1
Formula	C155H119Er2N16O21Pr
FW (g mol ^{_1})	3017.09
Wavelength (Å)	0.72932
<i>T</i> (K)	100
Crystal system	triclinic
Space group	<i>P</i> –1
a (Å)	16.3636(1)
b (Å)	19.5224(1)
<i>c</i> (Å)	23.3873(1)
α (°)	108.669(1)
β (°)	108.321(1)
γ (°)	92.112(1)
$V(A^3)$	6640.37(8)
Z	2
$ ho_{calcd}$ (g cm ⁻³)	1.508
μ (mm ⁻¹)	1.842
Reflections	35526
Rint	0.0425
Restraints	405
Parameters	1709
S	1.118
R1 [<i>I</i> >2 <i>o</i> (<i>I</i>)]	0.0562
$wR_2 [I > 2\sigma(I)]$	0.1733
R ₁ [all data]	0.0645
wR ₂ [all data]	0.1800
Largest peak / hole (e Å ³)	3.749 / -2.688

Table S2. Intramolecular metal...metal separations and bond lengths (Å) describing the coordination environments of the metal sites in the structure of compound **1**.

Pr1–O4 Pr1–O16 Pr1–O11 Pr1–O3 Pr1–O15 Pr1–O15 Pr1–O7 Pr1–O10 Pr1–N5 Pr1–N2 Pr1–N3	2.451 (3) 2.501 (3) 2.590 (2) 2.591 (2) 2.642 (2) 2.707 (3) 2.711 (2) 2.734 (3) 2.756 (3) 2.764 (3) 2.791 (3)	Er1–O9 E1–O5 Er1–O17 Er1–O6 Er1–O3 Er1–O1 Er1–O10 Er1–N1	2.264 (3) 2.300 (3) 2.310 (3) 2.334 (2) 2.339 (3) 2.351 (3) 2.378 (2) 2.401 (3)	Er2–012 Er2–08 Er2–015 Er2–011 Er2–018 Er2–013 Er2–07 Er2–N4	2.261 (3) 2.294 (3) 2.314 (3) 2.338 (3) 2.347 (3) 2.354 (2) 2.391 (2) 2.409 (3)
Pr1…Er1	3.9592(2)	Er1…Er2	7.9100 (2)	Er2…Pr1	3.9610 (2)

Table S3. Distances and angles describing the hydrogen bonds in the structure of compound **1** (see also Fig. S2).

D–H…A	D–H (Å)	H…A (Å)	D…A (Å)	D–H…A (°)			
O17–H17B⋯N1S	0.888(19)	1.84(2)	2.728(5)	174(5)			
O17–H17C⋯N2S	0.868(19)	1.86(2)	2.704(5)	165(5)			
O18–H18C…N3S	0.903(19)	1.87(3)	2.746(5)	164(5)			
O18–H18B…O13#1	0.903(19)	1.88(3)	2.740(4)	158(5)			
#1: 1-x, 1-y, 2-z							



Figure S1. View of the cation $[Er_2Pr(LA)_2(LB)_2(py)(H_2O)_2]^+$ of **1** with heteroatoms labelled (C atoms in grey). Only H atoms from H₂O ligands shown (in white). Hydrogen bonds with lattice pyridine molecules are shown as dashed black lines.



Figure S2. View of the structure of **1** highlighting hydrogen bonding interactions (dashed lines, see Table S3 for details).

Mass Spectrometry

Positive-ion ESI mass spectrometry experiments were performed by using a LC/MSD-TOF (Agilent Technologies) with a dual source equipped with a lock spray for internal reference introduction, at the Unitat d'Espectrometria de Masses from the Universitat de Barcelona. Experimental parameters: capillary voltage 4 kV, gas temperature 325° C, nebulizing gas pressure 103.42 kPa, drying gas flow 7.0 L min-1 and fragmentor voltage 175- 250 V. Internal reference masses were m/z 121.05087 (purine) or 922.00979 (HP-0921). Crystals of **1** were dissolved in mixtures of MeOH with the minimal amount of DMSO and introduced into the source by using a HPLC system (Agilent 110) with a mixture of H₂O/CH₃CN (1:1) as the eluent (200 µL min⁻¹). As observed previously for related clusters, the ionization caused the removal of both pyridine and water ligands from the complexes. Moleties related exclusively to the [ErPrEr] metal distribution were observed (Figures S3 to S6). Moreover, no signals for other metallic compositions were detected, thus evidencing not only the realization of the trinuclear heterometallic compound but also its robustness and exclusiveness in solution.



Figure S3. Selected region of the experimental (gray line) ESI-MS spectra of compound **1** ([ErPrEr]), emphasizing the $[Er_2Pr(LA)_2(LB)_2]^+$ fragment, together with the corresponding calculated signals for the [Pr₃] (purple line), [ErPr₂] (blue line), [Er₂Pr] (red line) and [Er₃] (green line), metal distributions.



Figure S4. Selected region of the experimental (gray line) ESI-MS spectra of compound **1** ([ErPrEr]), emphasizing the $[Er_2Pr(LA)_2(LB)_2]^+$ fragment, together with the corresponding calculated signal, emphasizing the correspondence with the isotopic distribution.



Figure S5. Selected region of the experimental (gray line) ESI-MS spectra of compound **1** ([ErPrEr]), emphasizing the ($[Er_2Pr(LA)_2(LB)_2]+H^+$)²⁺ (m/z = 1024.5845) fragment, together with the corresponding calculated signals for the [Pr₃] (purple line), [Pr₂Er] (blue line), [Er₂Pr] (red line) and [Er₃] (green line), metal distributions.



Figure S6. Selected region of the experimental (gray line) ESI-MS spectra of compound **1** ([ErPrEr]), emphasizing the ([$Er_2Pr(LA)_2(LB)_2$]+Na⁺)²⁺ (m/z = 1035.5858) fragment, together with the corresponding calculated signals for the [Pr₃] (purple line), [Pr₂Er] (blue line), [Er₂Pr] (red line) and [Er₃] (green line), metal distributions.

Analysis of the metal selectivity through DFT Studies

Ionic radii for Ln(III) ions

The collection of coordination-number-dependent ionic radii used for the Ln(III) ions in order to compute the Δr descriptor was taken from the study of Baloch et al.⁸, where a machine learning model was employed to expand Shannon's ionic radii⁹ to previously undescribed coordination numbers. Radius values were taken from the database provided by the authors (<u>https://cmd-ml.github.io/</u>).

As some radii for CN = 11 (Gd, Tb, Dy, Er, Tm, Yb, Lu) and CN = 12 (Er, Lu) were not available in the ML-expanded dataset, those values were interpolated from a simple 2-degree polynomial regression ($R = a(CN)^2 + b(CN) + c$, to account for the parabolic curvature of the points) to the set of ionic radii available for each Ln(III) ion. The r² values with this adjustment were above 0.99 for all metals in the dataset (Fig. S7).



Figure S7. Polynomial regressions (2-degree) for the coordination number of the Ln(III) ions against the ionic radii from Baloch et al.⁸

М	CN = 8	CN = 9	CN = 10	CN = 11	CN = 12
La	1.160	1.216	1.270	1.299	1.360
Ce	1.143	1.196	1.250	1.273	1.340
Pr	1.126	1.179	1.232	1.266	1.294
Nd	1.109	1.163	1.216	1.249	1.270
Sm	1.079	1.132	1.185	1.218	1.240
Eu	1.066	1.120	1.172	1.204	1.231
Gd	1.053	1.107	1.148	1.181	1.206
Tb	1.040	1.095	1.141	1.172	1.200
Dy	1.027	1.083	1.129	1.160	1.187
Но	1.015	1.072	1.120	1.147	1.174
Er	1.004	1.062	1.103	1.157	1.204
Tm	0.994	1.052	1.091	1.123	1.150
Yb	0.985	1.042	1.079	1.112	1.138
Lu	0.977	1.032	1.082	1.136	1.187

Table S4. Ionic radii in Å for Ln(III) ions, from Baloch et al.⁸ Values in italics correspond to polynomial interpolations on the original dataset.

The resulting values of $\Delta \mathbf{r}$ for the experimental complexes, together with the ΔR_{DFT} and a non-CN-corrected radius source from D'Angelo *et al.*¹⁰ are shown in Table S5.

Table S5. Radii-difference-based descriptors for experimental complexes (in Å), employing ML-based radii from Baloch et al.⁸ (Δr_{ML}), non-CN-corrected radii from D'Angelo et al.¹⁰ (Δr_{uncorr}) and *a posteriori* DFT-based median Ln – O distances (ΔR_{DFT})

Μ	Δr _{ML}	Δr_{uncorr}	ΔR_{DFT}
HoCeHo	0.258	0.165	0.301
ErPrEr	0.262	0.160	0.310
ErCeEr	0.269	0.180	0.296
YbCeYb	0.288	0.210	0.293
ErLaEr	0.295	0.210	0.337
LuCeLu	0.296	0.225	0.331

And we can compare the coordination number-corrected and uncorrected radii differences in Table S5 in a plot (Fig. S8).



Figure S8. Radii differences in experimental complexes from ML-based radii from Baloch et al. (Δr_{ML}), and from non-CN-corrected radii from D'Angelo et al. (Δr_{uncorr}).

Computational details

All geometries were fully optimized, without any constraint, using the ADF program (Scientific Computing and Modeling ADF2019.301¹¹). The BP86 functional, including the Becke¹² and Perdew¹³ gradient-corrected exchange and correlation functionals, was employed in all calculations. Regarding the basis set, TZP was used for the metal atoms, oxygen and nitrogen, while DZP was employed for carbon and hydrogen. To account for relativistic effects, the ZORA scalar relativistic Hamiltonian was employed¹⁴. This choice of a model was made in order to match previous studies on similar dimeric systems so as the resulting energies were directly comparable.

To reach proper SCF convergence, strong damping (density mixing step = 0.05) was used in all calculations. Additionally, to avoid convergence problems in early optimization steps (for both X-ray experimental structures and guesses for the non-isolated complexes), initial preoptimizations with a very low SCF convergence threshold $(1E^{-4})$ were performed for all structures, and then refined with the standard $1E^{-6}$ criterion for SCF convergence in geometry optimizations in ADF.

Data availability

The structures of the 25 optimized lanthanide trimeric complexes are available as a dataset collection in the ioChem-BD repository¹⁵ and can be accessed through the following link https://doi.org/10.19061/iochem-bd-1-227.

Electronic structure calculations: CASSCF-SO-RASSI approach

Given the complexity of the [ErPrEr] complex and the inability to describe *ab initio* the magnetic interactions between the lanthanide ions, we simplify the problem and study each of the metal centres separately. Thus, we have performed three different calculations where only one paramagnetic centre is considered, substituting the other two by diamagnetic analogues (erbium by lutetium and praseodymium by lanthanum). We then used the largest disorder component from the single crystal XRD structure to define our molecular geometries as [ErLaLu], [LuPrLu] and [LuLaEr]. Our results are derived from single point calculations at these structures and no geometry optimisation was performed.

The electronic structures of [ErLaLu], [LuPrLu] and [LuLaEr] (Tables S7-S9) were determined by means of CASSCF-SO-RASSI calculations using OpenMolcas.¹⁶ Basis sets from ANO-RCC library,^{17,18} were employed with VTZP quality for Er atoms, VDZP quality for coordinating atoms, and VDZ quality for all remaining atoms, employing the second-order DKH transformation. Cholesky decomposition of the two-electron integrals with a threshold of 10⁻⁸ was performed to save disk space and reduce computational demand. The molecular orbitals (MOs) were optimized in state-averaged CASSCF calculations within each spin manifold – details specific for Er and Pr ions are presented in Table S6. The resulting spin-orbit wavefunctions were decomposed into their crystal field wavefunctions, and the magnetisation curves and magnetic susceptibilities calculated using SINGLE_ANISO.¹⁹

The same methodology was applied to the previously reported [LuCeLu] compound to validate the approach against available experimental data on a monomeric paramagnetic compound.

Table S6. CASSCF-SO-RASSI details used to describe Er- (in [ErLaLu] and [LuLaEr]), Pr- (in [LuPrLu]) and Ce-based ([LuCeLu]) molecules. Grey scale associates the number of roots to a specific spin multiplicity.

	C	D	0-
	Er	Pr	Ce
Active space	(11.7)	(2.7)	(1,7)
(electrons, orbitals)			
Spin multiplicity	4	3	2
Spin multiplicity	2	1	-
CASSCE roots	35	21	7
CA330F 10015	112	28	-
DASSI rooto	35	21	7
NASSI 10015	114	28	-

Energy (cm ⁻¹)	Energy (K)	g1	g2	g3	Angle	Wavefunction
0.00	0.00	1.46	4.18	10.82		64% ±9/2⟩+11% ±13/2⟩+ 8% ±15/2⟩
12.94	18.62	1.45	2.31	11.70	8.22	42% ±11/2⟩+22% ±7/2⟩+ 21% ±15/2⟩
54.05	77.77	3.60	5.17	8.93	5.52	43% ±7/2⟩+14% ±15/2⟩+ 14% ±11/2⟩+7% ∓7/2⟩+ 5% ∓5/2⟩
134.62	193.69	2.78	4.11	7.62	84.36	58% ±5/2⟩+12% ∓7/2⟩+ 7% ±1/2⟩+7% ∓3/2⟩+ 6% ∓5/2⟩
187.46	269.71	2.28	4.76	9.26	53.17	$24\% \pm 3/2\rangle + 24\% \pm 13/2\rangle + 8\% \pm 1/2\rangle + 13\% \mp 3/2\rangle + 7\% \mp 1/2\rangle + 6\% \pm 15/2\rangle$
225.49	324.43	1.07	2.96	12.24	47.43	$24\% \pm 13/2\rangle + 20\% \pm 3/2\rangle +$ $11\% \pm 11/2\rangle + 10\% \pm 9/2\rangle +$ $8\% \pm 15/2\rangle$
267.65	385.09	0.62	0.92	14.87	34.56	33% ±15/2⟩+15% ±11/2⟩ +17% ±13/2⟩+7% ∓1/2⟩+ 6% ±9/2⟩
345.90	497.68	0.26	0.48	15.79	80.60	30% ±1/2⟩+21% ∓1/2⟩+ 15% ∓3/2⟩+7% ±3/2⟩

Table S7. Electronic structure of [ErLaLu] calculated with CASSCF-SO and quantised along the g3 direction of the ground doublet. Each row represents a Kramers doublet.

Table S8. Electronic structure of [LuPrLu] calculated with the CASSCF-SO and quantised along the g3 direction of the ground doublet. Each row represents an electronic state. Information on *g* tensors is obtained by defining MLTP 5; 2 2 2 2 1. Note that this is an approximation as the states are not degenerate (*ca* 20 cm⁻¹ energy shift).

E ^{CFPs} (cm ⁻¹)	E ^{CAS} (cm ⁻¹)	g3	Wavefunction
0.00	0.00	3.55	18% +4>+18% -4>+17% +1>+17% -1>+10% +3>+10% -3>
36.16	52.03	_	29% +4>+29% -4>+12% +2>+12% -2>+5% +1>+5% -1>
131.77	189.59	3.65	$17\% +2\rangle + 17\% -2\rangle + 14\% +3\rangle + 14\% -3\rangle + 9\% +4\rangle + 9\% -4\rangle + + 8\% 0\rangle + 7\% +1\rangle + 7\% -1\rangle$
155.04	223.07	_	10% 0 angle + 13% -1 angle + 13% +1 angle + 12% -2 angle + 12% +2 angle + 9% -3 angle + 9% +3 angle + 7% +4 angle + 7% -4 angle
168.79	242.85	1.66	$24\% +2\rangle + 24\% -2\rangle + 10\% +3\rangle + 10\% -3\rangle + 8\% +4\rangle + 8\% -4\rangle + 7\% 0\rangle + 4\% +1\rangle + 4\% -1\rangle$
195.10	280.71	_	$15\% +2\rangle + 15\% -2\rangle + 15\% +3\rangle + 15\% -3\rangle + 9\% +4\rangle + 9\% -4\rangle + 9\% 0\rangle + 8\% +1\rangle + 8\% -1\rangle$
292.04	420.18		27% +1>+27% -1>+20% 0>+12% +3>+12% -3>
332.30	478.11	- 5.00	$30\% 0\rangle + 14\% +2\rangle + 14\% -2\rangle + 11\% +3\rangle + 11\% -3\rangle + 9\% +4\rangle + 9\% -4\rangle$
417.20	600.26	-	$19\% +1\rangle + 19\% -1\rangle + 16\% +3\rangle + 16\% -3\rangle + 11\% +4\rangle + 11\% -4\rangle + 6\% 0\rangle$

Energy (cm ⁻¹)	Energy (K)	g1	g2	g3	Angle	Wavefunction
0.00	0.00	2.20	4.61	10.48		48% ±9/2⟩+10% ∓9/2⟩+ 7% ±13/2⟩+10% ±15/2⟩+ 7% ∓7/2⟩
16.90	24.32	1.75	3.55	9.31	12.03	$33\% \pm 7/2\rangle + 25\% \pm 11/2\rangle +$ $9\% \pm 15/2\rangle + 8\% \pm 9/2\rangle +$ $6\% \mp 9/2\rangle$
54.01	77.71	3.24	4.58	10.00	16.44	28% ±7/2⟩+14% ±15/2⟩+ 32% ±11/2⟩+7% ±9/2⟩+ 9% ∓5/2⟩
113.57	163.40	0.83	2.74	10.47	86.52	$50\% \pm 5/2 angle + 11\% \mp 7/2 angle +$ $10\% \pm 3/2 angle + 9\% \mp 1/2 angle +$ $8\% \mp 5/2 angle + 7\% \pm 7/2 angle$
168.63	242.62	0.84	3.95	9.57	86.71	$45\% \pm 3/2 angle + 9\% \pm 13/2 angle + 6\% \pm 1/2 angle + 11\% \mp 5/2 angle + 6\% \mp 1/2 angle$
220.78	317.66	0.57	3.88	11.19	20.96	31% ±13/2⟩+14% ∓13/2⟩ +12% ±1/2⟩+5% ±11/2⟩+ 11% ±9/2⟩
269.70	388.04	1.75	2.01	11.89	18.09	$40\% \pm 15/2 angle + 14\% \pm 11/2 angle$ + 15% ±13/2 angle + 8% ∓1/2 angle + 6% ±1/2 angle
321.21	462.15	0.53	1.16	14.93	71.02	$32\% \pm 1/2 angle + 11\% \mp 1/2 angle +$ $7\% \mp 3/2 angle + 12\% \pm 3/2 angle +$ $11\% \pm 15/2 angle + 9\% \pm 13/2 angle$

Table S9. Electronic structure of [LuLaEr] calculated with CASSCF-SO and quantised along the g3 direction of the ground doublet. Each row represents a Kramers doublet.

Table S10. Electronic structure of [LuCeLu] calculated with CASSCF-SO and quantised along the g3 direction of the ground doublet. Each row represents a Kramers doublet.

Energy (cm ⁻¹)	Energy (K)	g1	g2	g3	Angle	Wavefunction
0.00	0.00	0.64	0.71	3.24		60% ±5/2)+19% ∓5/2)+ 17% ∓1/2)
74.21	106.77	0.13	0.50	3.35	13.4	$45\% \pm 1/2 angle + 28\% \mp 3/2 angle +$ $12\% \pm 5/2 angle + 10\% \pm 3/2 angle$
258.95	372.57	1.11	1.38	2.70	78.4	58% ±3/2)+25% ∓1/2)+ 9% ±1/2)+6% ∓5/2)



Figure S9. Schematic representation (two views) of the g3 vectors within the molecular frame of [ErPrEr] (1), obtained from independent calculations on [ErLaLu], [LuPrLu] and [LuLaEr]. The g-vectors associated with Er are parallel to each other (lie within a plane that splits the molecule in half through the nitrogen atom of the Pr-coordinating pyridine) – the angle between this plane's normal and Pr's g-vector is 21.5 degrees. For clarity's sake, naphthalene of H₂LA and H₂LB are hidden and only hydrogen atoms of coordinating water are shown.

To assess the calculated electronic structure of each of the Er and Pr ions separately, we compare our results to the previously reported [ErLaEr] (6) and [LuCeLu] (5) as well as the new [ErPrEr] (1) compounds. The first two represent systems where the intramolecular magnetic interactions can be safely neglected, and their magnetic properties can be approximated as a sum of the ions that constitute them. As such, Figs. S10-S12 report the comparison between experimental and calculated magnetisation curves and susceptibilities traces. For [ErLaEr] (6, Fig. S10), we observe a very good agreement at low temperatures (in the susceptibility) and low fields (< 1 T, in the magnetisation curves), which progressively deviates. This indicates that the description of the ground doublet is accurate, further confirmed by the g-values (Table S7 and Table S9), which agree with those extracted from EPR (CASSCF: [1.5, 4.2, 10.8] for [ErLaLu], [2.2, 4.6, 10.5] for [LuLaEr]; EPR for [ErLaEr] (6) :[1, 5±0.3, 11.5±0.3).²⁰ However, the disagreement at high temperatures and fields suggests that the CASSCF results underestimate the energy separation of the excited states, meaning that the contributions from excited states are artificially exaggerated. Indeed, fitting the susceptibility traces to a two-doublets model yields an energy separation of 77 K²⁰, whereas CASSCF predicts the first excited state at *ca.* 20 K (Table S7 and Table S9). This is likely to result from differences on the position of the coordinating water between experimental conditions and that considered for our calculations.^{21,22} It is worth noting that the disagreement might arise from intermolecular interactions, as Er...Er distances are the shortest between molecular units (Fig. S2), which is not described by our calculations. Similarly, Fig. S11 presents the comparison for [LuCeLu] (5), showing a good agreement, yet slightly overestimated - again, this might be attributed to CASSCF underestimating the energy gap to the first excited state (107 K), as compared to that extracted from xT (210 K).²⁰ Interestingly, our CASSCF results seem to predict a wrong g-tensor for the ground doublet, predicted to be highly anisotropic in sharp contrast to the isotropic experimental EPR.²⁰ However, using the CASSCF-SO highly anisotropic g-tensor reproduces very well the magnetisation curves (Fig. S11). Finally, the magnetic properties of [ErPrEr] (1) compound have also been approximated as a simple sum of the individual contributions (Fig. S12) - this is clearly incorrect as the intramolecular magnetic interactions, though likely weak, are completely overlooked, but it still offers some valuable information. For instance, the high-field magnetisation curves agree very well, indicating that the ground states of the ions are well described when the weak magnetic interactions become irrelevant (when the Zeeman effect dominates). All the commented CASSCF shortcomings could be addressed by expanding the considered active space and/or including dynamical correlation, but the molecules' sizes make this practically impossible. Still, we can confidently conclude that the applied methodology can satisfactorily capture the macroscopic magnetic properties of the investigated compounds.



Figure S10. Comparison of experimental (dots) and CASSCF-SO calculated (solid lines) χT versus *T* traces of [ErLaEr] (**6**) under 1000 Oe dc field. The inset shows the comparison for magnetization curves at 2, 5 and 10 K. The calculated traces are simply the sum of individual [ErLaLu] and [LuLaEr] traces.



Figure S11. Comparison of experimental (dots), CASSCF-SO (solid lines) and S=1/2 calculated (dashed lines) magnetisation curves of [LuCeLu] (**5**) at 2 and 5 K. Dashed lines are obtained assuming an S=1/2 centre with the g-values calculated from CASSCF-SO (Table 5) in PHI.²³



Figure S12. Comparison of experimental (dots) and CASSCF-SO calculated (solid lines) χT versus *T* traces of [ErPrEr] (**1**) under 1000 Oe dc field. The inset shows the comparison for magnetization curves at 2 and 5 K (also shown in Fig. 5 of the main text). The calculated traces are naively approximated as the sum of individual [ErLaLu], [LuPrLu] and [LuLaEr] traces.

EPR spectroscopy

Continuous-wave (CW) electron paramagnetic resonance (EPR) measurements were performed on a Bruker EMXplus EPR spectrometer operating at X-band (*ca.* 9.4 GHz). The magnetic field values were corrected against Bruker's strong pitch standard sample (g = 2.0028). Frozen solution spectra were recorded on 5 mM solution of **1** dissolved in a mixture of the deuterated solvents methanol/ethanol/dmso (90:10:1 v/v/v). Pulse experiments were performed with a Bruker ElexSys E580 spectrometer operating at X-band (*ca.* 9.7 GHz). Echo-detected field swept (EDFS) spectra were collected using a two-pulse Hahn-echo sequence ($\pi/2 - \tau - \pi - \tau$ – echo) at fixed interpulse delay time τ and scanning the magnetic field. Pulse EPR measurements were recorded from both 5 and 2.5 mM solutions at 3 to 6 K. Cryogenic temperatures were achieved using a cryogen-free closed-cycle helium circuit and the EasySpin software was used to simulate the spectra.²⁴

Phase memory times (gathered in Table S11) were measured using a Hahn echo sequence and varying the interpulse delay 2τ at a fixed magnetic field. Long selective pulses (up to 400 ns) were often used to suppress electronic spin-echo envelope modulation (ESEEM) effects from proton and deuterium nuclei. The curves were fitted with the exponential equation S1,

$$Y(2\tau) = Y(0)exp\left[\left(-\frac{2\tau}{T_m}\right)\right]$$
(S1)

or, for strongly modulated data, equation S2:

$$Y(2\tau) = Y(0)exp\left[\left(-\frac{2\tau}{T_m}\right)^{\beta}\right](1 + ksin(\omega\tau + \phi))$$
(S2)

where $Y(2\tau)$ is the echo integral for a pulse separation τ , Y(0) is the echo intensity extrapolated to $\tau = 0$, β is the stretch factor, *k* is the modulation depth, ω is the Larmor angular frequency of a nucleus coupled to the electron spin and ϕ is the phase correction.

Spin-lattice relaxation times (gathered in Table S11) were measured using an inversion recovery sequence $(\pi - t - \pi/2 - \tau - \pi - \tau - \text{echo})$ and varying the interpulse delay *t* at a fixed magnetic field and τ . The curves were fitted with the biexponential equation (equation S3), where the fast component is attributed to spectral diffusion, T_{SD} , which is commonly one order of magnitude smaller than T_1 :

$$Y(2\tau) = Y_{SD}ex p\left(-\frac{t}{T_{SD}}\right) + Y_1ex p\left(-\frac{t}{T_1}\right)$$
(S3)

Rabi oscillations were detected using a transient nutation pulse sequence $(t_p - t - \pi/2 - \tau - \pi - \tau - \text{echo})$ and varying the tipping pulse length, t_p . The oscillation curves were baselined with a polynomial function and the Rabi frequency, Ω_R , was determined by applying Fourier Transform.



Figure S13. Variation of the normalised echo intensities as a function of the interpulse delay 2τ for a 2.5 mM solution of **1** at 3 K. Lines represents the best fits to an exponential decay function (equation S1).



Figure S14. Variation of the normalised echo intensities as a function of the interpulse delay 2τ for a 2.5 mM solution of **1** at 3 K. Lines represents the best fits to an exponential decay function including modulation (equation S2).



Figure S15. Inversion recovery data as a function of the interpulse delay *t* for a 2.5 mM solution of **1** at a) 3 K and b) 5.0 K (scatter) and fits to a biexponential function (equation S3, lines).



Figure S16. Inversion recovery data as a function of the interpulse delay t of a 5 mM solution of **1** at 3 K (scatter) and fits to a biexponential function (equation S3, lines).

Table S11. Parameters that provide the best fits to ESE detected Inversion Recovery signals and the 2p-ESE decay in Figures S13-S16. Asterisks (*) indicate data acquired at T = 5 K, the rest being obtained at T = 3 K.

Concentration	<i>B</i> (mT)	T ₁ (μs)	T _{SD} (μ s)	T _M (μs)
2.5 mM	145			0.568(10)
	185	258(6)	36(1)	0.354(2)
	200	242(4)*	37(1)*	0.393(2)
	330	297(2)	43(1)	0.638(4)
		131(1)*	22.5(2)*	
	400	99.5(7)*	13.42(5)*	0.566(8)
	510	72.1(7)*	7.93(3)*	0.494 (3)
	700			0.389(1)
	1000			0.223(5)
5 mM	185	92(1)	15 3(2)	
0 min	266	119 2(7)	19.3(2)	
	330	128.4(7)	20.1(2)	
	400	81.7(7)	17.0(2)	
	510	79.0(̀8)́	13.5(1)́	
	700	113.3(8)	11.1(1)	
		* <i>T</i> = 5 K	• •	



Figure S17. Rabi oscillations for a 2.5 mM solution of **1** at 3 K acquired at 3300 G: (a) nutation data at two mw attenuations; (b) Fourier transforms of nutation data; (c) B_1 dependence of the Rabi frequency. The solid line is a guide to the eye, emphasizing the linear dependence expected for qubits. The peak at 14.05 MHz is associated with the nuclear modulation of ¹H.

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