

Supporting Information For:

Variations in the local Co^{II} geometry of four triangular L₃Co₃^{II}Ln^{III} complexes

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Table of Contents

Synthetic Procedures	S2
General Procedures	S2
General procedure for the preparation of complexes C1 – C4:	S2
Table S1.	S3
Figure S1.	S4
Figure S2.	S5
References	S6

Synthetic Procedures

General Procedures

All experiments were carried out in air. Solvents and reagents were used as received from commercial sources (Merck/Sigma-Aldrich, ThermoFisher) without further purification. The synthesis of ligand **H₂L** has recently been reported¹ and was adapted from the method originally reported by MacLachlan et al.² IR spectra were collected on a Nicolet 5700 FT-IR spectrometer with an ATR sampling accessory. Elemental analyses were determined by the Campbell Microanalytical Laboratory at the University of Otago.

Single-crystal X-ray diffraction experiments were carried out on a Bruker D8 Venture diffractometer equipped with an I μ S Diamond microfocus Cu-K α source ($\lambda = 1.54187 \text{ \AA}$) and a Photon III detector. Single crystals were mounted on MiTeGen mylar loops using Fomblin Y $\text{\textcircled{R}}$ and cooled to 100 K with an Oxford Cryostream 800. Data was collected and processed using the APEX3 software package.³ The structures were solved by intrinsic phasing with SHELXT⁴ and refined against least squares using SHELXL,⁵ as implemented in Olex2.⁶ Non-hydrogen atoms were refined anisotropically and hydrogen atoms were calculated to their ideal positions unless otherwise stated and refined using a riding model with fixed U_{iso} values. Crystal structure and refinement details for **C1** – **C4** can be found in Table S1, ESI. CCDC deposition numbers 2105529 – 2105532.

Magnetisation and magnetic susceptibility measurements were carried out with a Quantum Design MPMS-XL7 SQUID magnetometer. Measurements were corrected with diamagnetic blank data from the empty sample holder. The diamagnetic contribution of the sample itself was estimated using Pascal's constants. To avoid possible field-alignment effect, the polycrystalline samples were fixed with a small amount of eicosane.

General procedure for the preparation of complexes C1 – C4: Co(NO₃)₂·6H₂O (145 mg, 0.5 mmol) was reacted with **H₂L** (108 mg, 0.5 mmol) and the corresponding lanthanide salt (0.167 mmol) in methanol (10 mL) in a 3:3:1 equivalence. Each mixture was stirred overnight to allow complete dissolution, then filtered, and diethyl ether was allowed to passively diffuse into the methanolic solutions. Crystal yields are calculated based on the masses harvested after 2-3 weeks, however, the filtrate can be resubjected to diethyl ether to yield another crop of the same crystals over a much longer period – typically 3+ months. No melting point was observed when crystalline samples of each complex were heated to 350 °C. Solvent contained within square brackets after the main complex denote species within the solvent mask.

C1 [L₃Co₃Dy(NO₃)₂(H₂O)(MeOH)₅](NO₃): Orange blocky crystals, 58% yield based on Dy(NO₃)₃·6H₂O. ATR-IR ν : 1614, 1566, 1483, 1435, 1378, 1351, 1310, 1260, 1124, 1027, 969, 753, 682 cm⁻¹. Microanalytical data found(calc) for **C1** (calculated for C₄₁H₄₀Co₃DyN₃O₂₇, M_r = 1346.06 g mol⁻¹) C: 36.30(36.58), H:3.32(3.00), N: 3.22(3.12).

C2 [L₃Co₃Gd(NO₃)₃(MeOH)₄]: Orange blocky crystals, 51% yield based on Gd(NO₃)₃·6H₂O. ATR-IR ν : 1611, 1567, 1486, 1432, 1382, 1351, 1313, 1259, 1141, 1029, 975, 753, 697 cm⁻¹. Microanalytical data found(calc) for **C2** (calculated for C₄₀H₃₄Co₃GdN₃O₂₅, M_r = 1290.75 g mol⁻¹) C: 36.99(37.22), H:2.92(2.66), N: 3.31(3.26).

C3 [L₃Co₃La(NO₃)₂(H₂O)₆](NO₃)(H₂O)·[1.5Et₂O]: Orange plate-like crystals, 57% yield based on La(OAc)₃·6H₂O. ATR-IR ν : 1615, 1566, 1482, 1435, 1378, 1351, 1311, 1261, 1128, 1027, 969, 753, 682 cm⁻¹. Microanalytical data found(calc) for **C3** (calculated for C₃₆H₃₂Co₃LaN₃O₂₈, M_r = 1270.35 g mol⁻¹) C: 34.30(34.04), H:2.32(2.54), N: 3.32(3.31).

C4 [L₃Co₃TbCl(NO₃)₂(H₂O)_{0.5}(MeOH)_{3.5}]·[2.5H₂O]: Orange blocky crystals, 66% yield based on TbCl₃·6H₂O. ATR-IR ν : 1611, 1568, 1486, 1432, 1382, 1352, 1313, 1259, 1141, 1030, 974, 755, 711

cm⁻¹. Microanalytical data found(calc) for **C4** (calculated for C_{39.5}H₃₈ClCo₃N₂O_{24.5}Tb, M_r = 1303.90 g mol⁻¹) C: 36.51(36.38), H:2.60(2.94), N: 2.00(2.15).

Table S1. Crystal structure and refinement details for complexes **C1** – **C4**. CCDC deposition numbers 2105529 – 2105532.

Complex	C1 Dy	C2 Gd	C3 La	C4 Tb
CCDC Number	2105529	2105530	2105531	2105532
Molecular Formula	C ₄₁ H ₄₀ Co ₃ DyN ₃ O ₂₇	C ₄₀ H ₃₄ Co ₃ GdN ₃ O ₂₅	C ₄₂ H ₄₇ Co ₃ LaN ₃ O _{29.5}	C _{39.5} H ₃₆ Co ₃ TbClN ₂ O _{23.5}
Formula weight	1346.05	1290.74	1381.52	1285.86
T [K]	100	100	100	100
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	10.2212(8)	10.1882(12)	10.2888(8)	14.0045(5)
<i>b</i> [Å]	11.0914(10)	10.2651(13)	15.4555(13)	15.7554(5)
<i>c</i> [Å]	22.1617(19)	23.231(3)	16.0338(14)	41.1854(16)
α [°]	91.217(7)	86.370(8)	93.324(7)	90
β [°]	91.740(6)	84.284(8)	108.261(8)	96.063(2)
γ [°]	116.345(3)	65.297(8)	90.444(6)	90
<i>V</i> [Å ³]	2248.7(6)	2195.7(5)	2416.3(4)	9036.6(6)
<i>Z</i> (<i>Z'</i>)	2(1)	2(1)	2(1)	8(1)
ρ_{calc} [g cm ⁻³]	1.988	1.952	1.899	1.890
μ [mm ⁻¹]	18.174	19.214	15.544	17.370
<i>F</i> (000)	1340	1280	1388	5104
Size [mm]	0.18 x 0.18 x 0.14	0.17 x 0.16 x 0.14	0.14 x 0.10 x 0.04	0.12 x 0.10 x 0.10
Radiation	CuK α (λ = 1.54178 Å)	CuK α (λ = 1.54178 Å)	CuK α (λ = 1.54178 Å)	CuK α (λ = 1.54178 Å)
2 θ range [°]	3.992 to 136.472	3.824 to 136.488	5.730 to 136.492	8.474 to 136.468
Reflns	22277	76045	34920	36728
Ind. reflns	8044	7796	8664	8148
Restraints / Parameters	15 / 698	12 / 666	91 / 681	21 / 645
Goof on <i>F</i> ²	1.043	1.134	1.036	1.029
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0873 <i>wR</i> ₂ = 0.2074	<i>R</i> ₁ = 0.0590 <i>wR</i> ₂ = 0.1432	<i>R</i> ₁ = 0.0804 <i>wR</i> ₂ = 0.2016	<i>R</i> ₁ = 0.0546 <i>wR</i> ₂ = 0.1292
Final <i>R</i> indices [all data]	<i>R</i> ₁ = 0.1414 <i>wR</i> ₂ = 0.2413	<i>R</i> ₁ = 0.0936 <i>wR</i> ₂ = 0.1602	<i>R</i> ₁ = 0.1199 <i>wR</i> ₂ = 0.2235	<i>R</i> ₁ = 0.0924 <i>wR</i> ₂ = 0.1479
Residual density [e Å ⁻³]	1.39 / -1.64	0.87 / -1.17	1.85 / -1.17	1.07 / -1.26

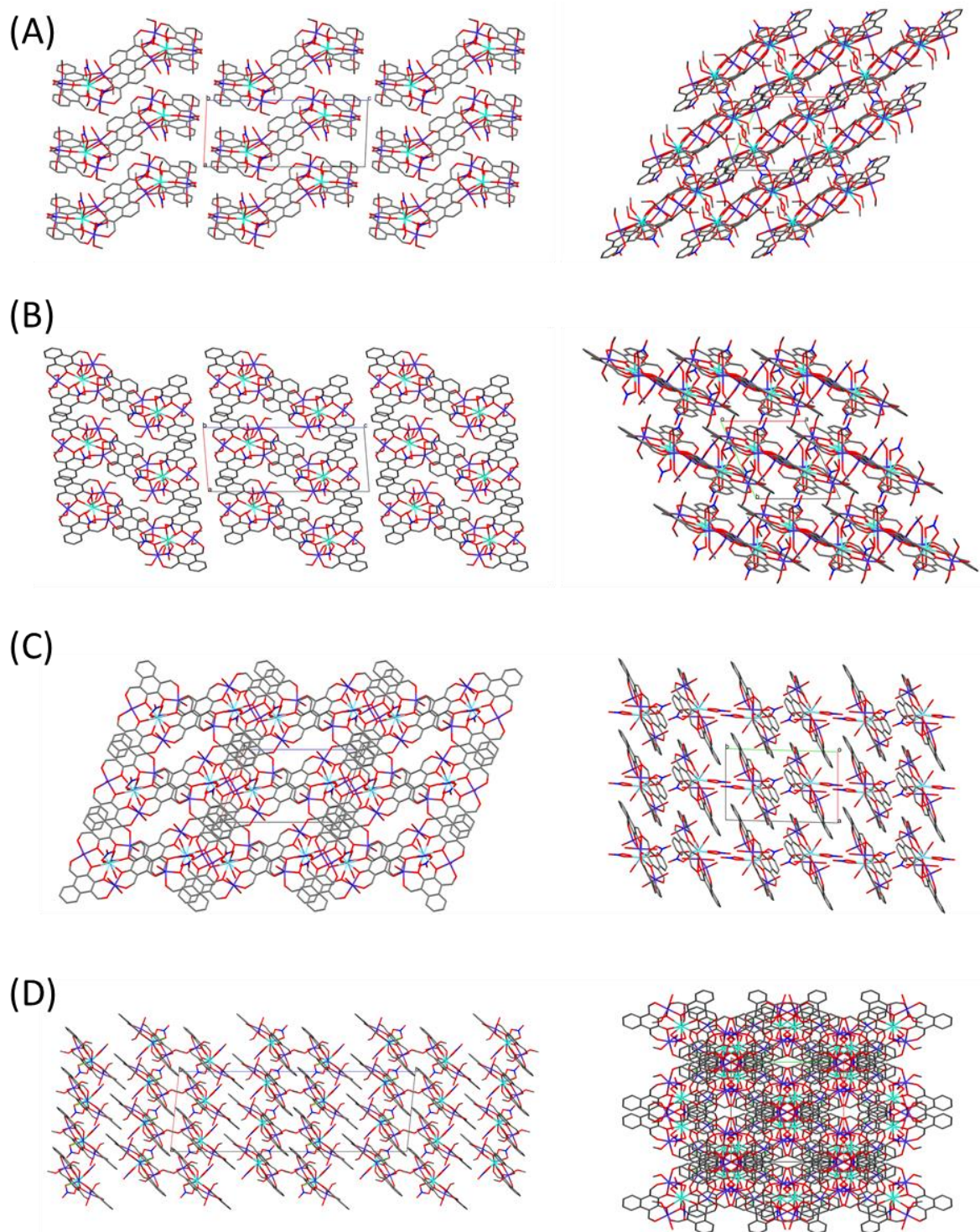


Figure S1. X-ray crystal structure packing diagrams viewed along the crystallographic *b*-axis (left) and *c*-axis (right) of **C1** (A), **C2** (B), **C3** (C), and **C4** (D). H atoms, disordered species, and non-coordinated species have been omitted for clarity. C = grey, Cl = green, Ln = turquoise, O = red, N = blue.

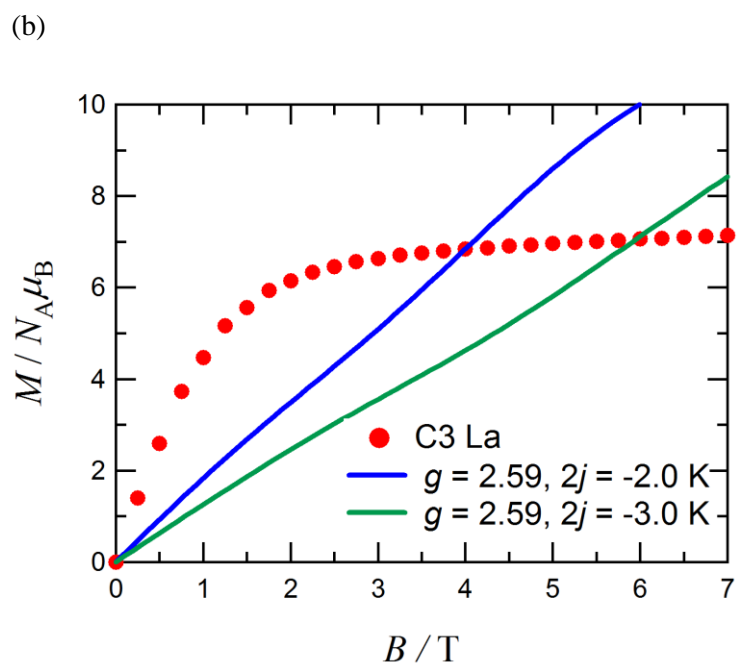
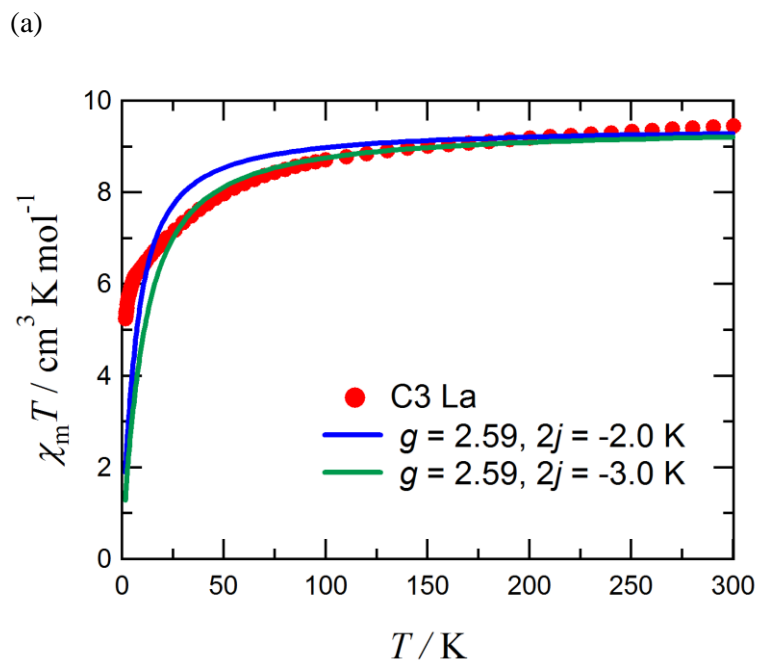


Figure S2. Simulation⁶ of the $\chi_m T(T)$ and $M(H)$ data on **C3** based on the following spin Hamiltonian: $H = -2j(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_3 \cdot \mathbf{S}_1)$. The parameters are as follows: $2j_{\text{Co-Co}}/k_B = -2.0$ and -3.0 K and $g_{\text{avg}} = 2.59$.

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