

SUPPORTING INFORMATION

for

By Design: A Macrocyclic 3d-4f Single-Molecule Magnet with Quantifiable Zero-Field Slow Relaxation of Magnetization

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Supplementary X-ray data

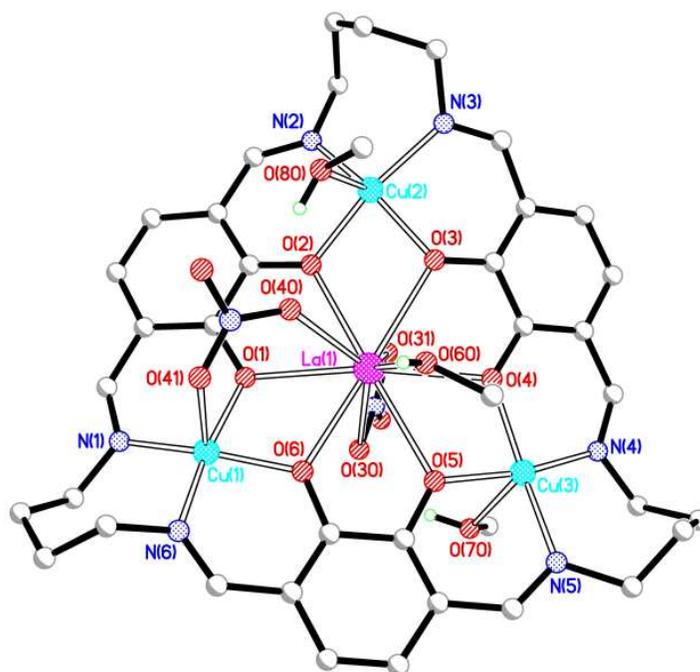


Figure S1: The crystal structure of $[\text{Cu}_3\text{La}(\text{L}^{\text{Bu}})(\text{NO}_3)_2(\text{MeOH})_3](\text{NO}_3)$. For clarity, non-acidic hydrogen atoms and the non-coordinated nitrate anion have been omitted.

Structure description for $[\text{Cu}_3\text{La}(\text{L}^{\text{Bu}})(\text{NO}_3)_2(\text{MeOH})_3](\text{NO}_3)$: Overall, the structure of $[\text{Cu}_3\text{La}(\text{L}^{\text{Bu}})(\text{NO}_3)_2(\text{MeOH})_3](\text{NO}_3)$ is very similar to the terbium(III) analogue, with the large lanthanum(III) ion bound in the central O_6 cavity and the smaller copper(II) ions in the outer N_2O_2 sites. The lanthanum(III) ion is ten-coordinate, with distorted decahedral geometry. All three copper(II) ions are all five-coordinate and are fairly regular square pyramids¹ (τ for $\text{Cu}(1) = \text{Cu}(3) = 0.15$; $\text{Cu}(2) = 0.20$). One of the nitrate anions is bound in a bidentate fashion to the lanthanum(III) ion, one bridges the lanthanum(III) ion and a copper(II) in a μ -mode and the remaining anion is not coordinated. One methanol molecule is coordinated to the lanthanum(III) ion and two are coordinated in the apical position of two copper(II) ions. The macrocycle is quite curved; the angles made by the plane of an arbitrarily chosen catecholate ring with the planes of the other two rings are 18.8° and 39.4° .

Refinement details for $[\text{Cu}_3\text{La}(\text{L}^{\text{Bu}})(\text{NO}_3)_2(\text{MeOH})_3](\text{NO}_3)$: All hydrogen atoms were placed in calculated positions and rode on the attached non-H atom with $U(\text{H})=1.2U(\text{X})$. In the case of $\text{X} = \text{O}$, the hydrogen selected was the one that formed the best hydrogen bond. All non-H atoms were refined anisotropically except for two catecholate carbon atoms (C4, C16) that presented negative ellipsoid parameters unless refined isotropically. An ISOR restraint was used on four carbon atoms (C6, C14, C20, C27) with a low principal mean square atomic displacement. No disorder is present. For further details see the cif file.

Refinement details for $[\text{Cu}_3\text{Tb}(\text{L}^{\text{Bu}})(\text{NO}_3)_2(\text{DMF})(\text{H}_2\text{O})](\text{NO}_3)\cdot\text{DMF}$: All hydrogen atoms were placed in calculated positions and rode on the attached non-H atom with $U(\text{H})=1.2U(\text{X})$. In the case of $\text{X} = \text{O}$, the hydrogen selected was the one that formed the best hydrogen bond. All non-H atoms were refined anisotropically except for two partial-occupancy carbonyl oxygen atoms (O80, O90) of the non-coordinated DMF solvent molecules. For further details see the cif file.

Supplementary magnetic data

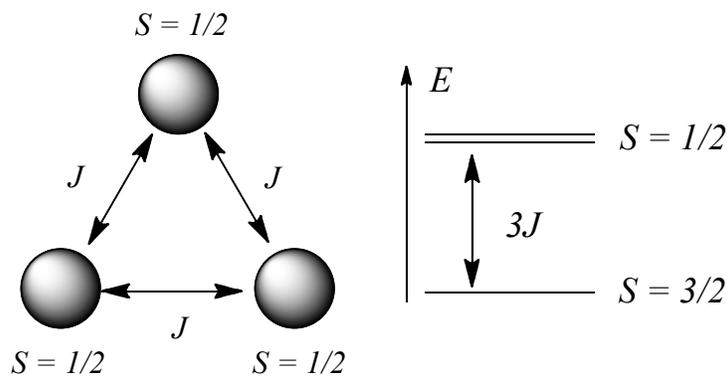


Figure S2: Scheme of the spin topology in $[\text{Cu}_3\text{La}(\text{L}^{\text{Bu}})]$ and its energy diagram in the case of ferromagnetic superexchange interactions.

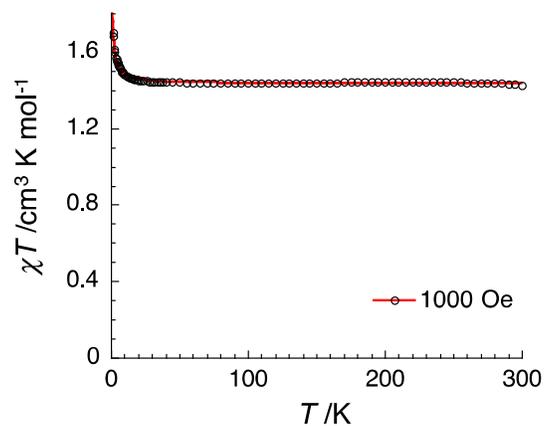


Figure S3: Temperature dependence of the χT product of $[\text{Cu}_3\text{La}(\text{L}^{\text{Bu}})]$ in a 1000 Oe dc field (circles) and a fit to the data (redline) based on the model shown in Figure S2.

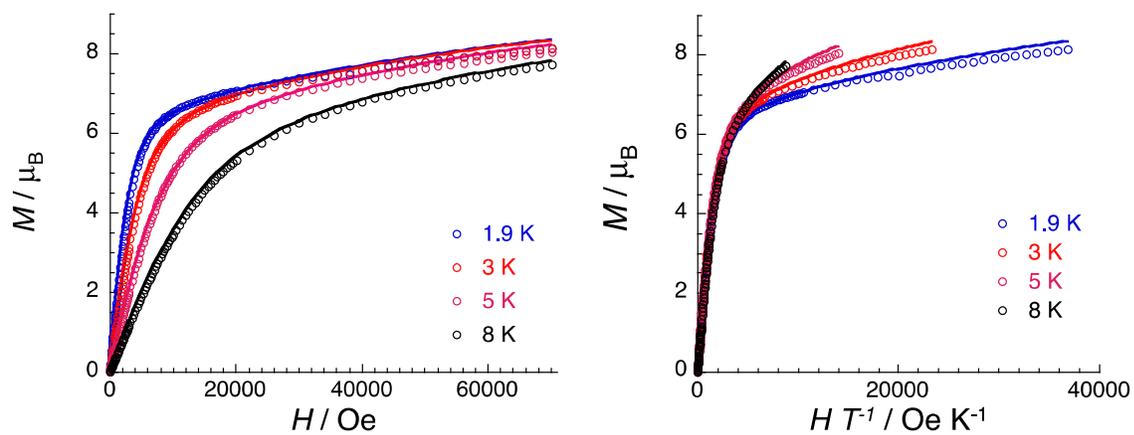


Figure S4: M vs. H (left) and M vs. H/T (right) data for $[\text{Cu}_3\text{Tb}(\text{L}^{\text{Bu}})]$ at the indicated temperatures, scanning at about $100 - 200 \text{ Oe min}^{-1}$. The solid lines are the calculated magnetization from the ab initio calculations described in the text.

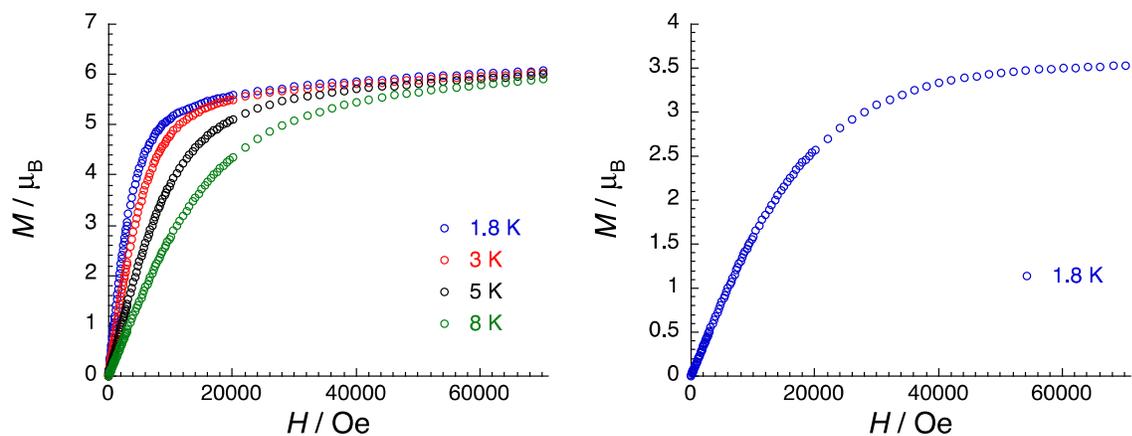


Figure S5: Field dependence of magnetisation for $[\text{Zn}_3\text{Tb}(\text{L}^{\text{Bu}})]$ (left) and $[\text{Cu}_3\text{La}(\text{L}^{\text{Bu}})]$ (right) at the temperatures indicated, scanning at about $100\text{-}200 \text{ Oe min}^{-1}$.

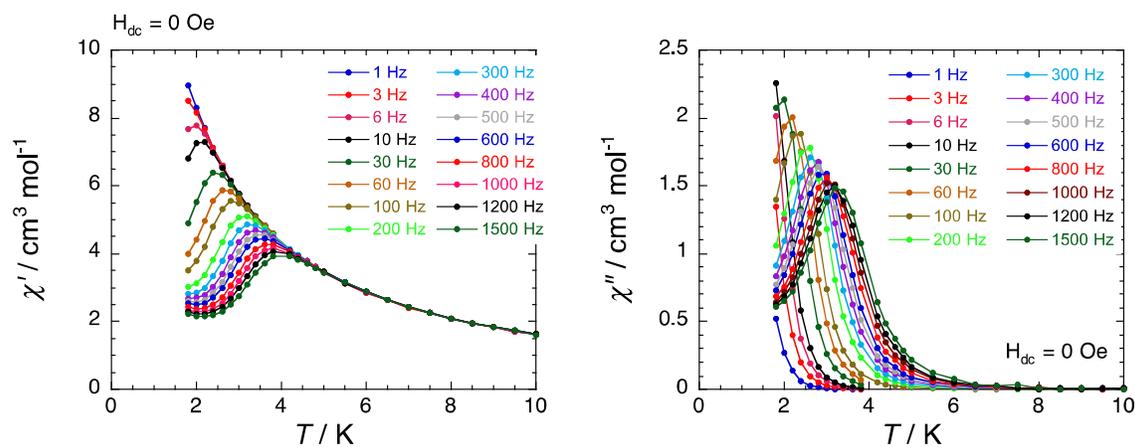


Figure S6: Temperature dependence of the in-phase (left) and out-of-phase (right) components of the ac susceptibility for $[\text{Cu}_3\text{Tb}(\text{L}^{\text{Bu}})]$ at the frequencies indicated in zero-dc field.

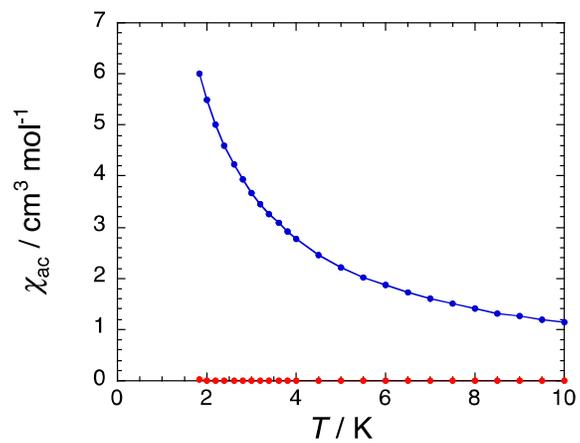


Figure S7: Temperature dependence of the in-phase and out-of-phase components of ac susceptibility for $[\text{Zn}_3\text{Tb}(\text{L}^{\text{Bu}})]$ at 1000 Hz in zero-dc field.

Additional ab initio results

Table S1. A comparison of low-lying level energies (in cm^{-1}) corresponding to the free ion $J = 6$ multiplet of central Tb ions in $[\text{Cu}_3\text{Tb}(\text{L}^{\text{Pr}})]$ and $[\text{Cu}_3\text{Tb}(\text{L}^{\text{Bu}})]$. The states defining the axiality are shown with bold: the axiality of Tb ion increases with the decrease of the energy gap.

$[\text{Cu}_3\text{Tb}(\text{L}^{\text{Pr}})]$	$[\text{Cu}_3\text{Tb}(\text{L}^{\text{Bu}})]$
0.000	0.000
4.248	0.174
59.496	42.060
91.321	42.688
102.018	76.038
153.304	86.706
164.914	109.163
211.549	110.691
220.366	128.768
264.691	182.476
267.049	185.891
472.033	406.847
472.968	407.827
...	...

Table S2. Calculated exchange energies (in K) and the corresponding g tensors of the low-lying exchange Kramers doublets of the previously reported $[\text{Cu}_3\text{Tb}(\text{L}^{\text{Pr}})]$ complex² and the present $[\text{Cu}_3\text{Tb}(\text{L}^{\text{Bu}})]$ compounds.

	$[\text{Cu}_3\text{Tb}(\text{L}^{\text{Pr}})]^{4\text{d}}$			$[\text{Cu}_3\text{Tb}(\text{L}^{\text{Bu}})]$		
$J(\text{Cu-Cu})/k_{\text{B}}$	1.41 K			1.37 K		
$J(\text{Cu-Tb})/k_{\text{B}}$	4.14 K			4.34 K		
Kramers Doublets	energy cm^{-1}	g tensor		energy cm^{-1}	g tensor	
1	0.000	g_{X}	0.0702	0.000	g_{X}	0.0018
		g_{Y}	0.0849		g_{Y}	0.0021
		g_{Z}	22.5796		g_{Z}	23.9647
2	7.105	g_{X}	2.3663	8.333	g_{X}	0.0906
		g_{Y}	2.7211		g_{Y}	0.1029
		g_{Z}	16.3099		g_{Z}	19.7233
3	9.064	g_{X}	1.0807	10.220	g_{X}	0.0433
		g_{Y}	1.3485		g_{Y}	0.0509
		g_{Z}	16.5745		g_{Z}	19.7362
4	9.068	g_{X}	1.1312	10.453	g_{X}	0.0457
		g_{Y}	1.3429		g_{Y}	0.0536
		g_{Z}	16.4972		g_{Z}	19.7366
5	16.026	g_{X}	1.8793	16.988	g_{X}	0.0207
		g_{Y}	2.6203		g_{Y}	0.1785
		g_{Z}	11.9709		g_{Z}	15.4856
6	17.920	g_{X}	0.9637	18.916	g_{X}	0.0253
		g_{Y}	1.2247		g_{Y}	0.0740
		g_{Z}	12.2555		g_{Z}	15.5022
7	17.924	g_{X}	0.9765	19.147	g_{X}	0.0227
		g_{Y}	1.1664		g_{Y}	0.0718
		g_{Z}	12.1787		g_{Z}	15.5025
8	23.608	g_{X}	0.1508	26.027	g_{X}	0.0066
		g_{Y}	0.1766		g_{Y}	0.0369
		g_{Z}	9.5883		g_{Z}	11.2530

References

1. A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Vershoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349-1356.
2. H. L. C. Feltham, R. Clérac, L. Ungur, V. Vieru, L. F. Chibotaru, A. K. Powell and S. Brooker, *Inorg. Chem.*, 2012, **51**, 10603–10612.