ELECTRONIC SUPPORTING INFORMATION (ESI)

A New Family of Heterometallic [Cu_6M_4] (M = Gd, Tb, Dy and Y) Clusters Derived from the Combined use of Selected Pyridyl Poly-alcohol Ligands

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Single crystal X-Ray crystallography

Table S1. Crystal data and structural refinement parameters for compounds **1**·3MeCN, **2**·3MeCN, **3**·4MeCN and **4**·4MeCN.

Identification code	**1**·3MeCN	**2**·3MeCN	**3**·4MeCN	**4**·4MeCN
Empirical formula	$C_{74}H_{89}Cu_6Gd_4N_{19}O_{44}$	$C_{74}H_{89}Cu_6Tb_4N_{19}O_{44}$	$C_{76}H_{92}Cu_6Dy_4N_{20}O_{44}$	$C_{76}H_{92}Cu_6Y_4N_{20}O_{44}$
Formula weight	2958.88	2965.56	3020.93	2726.57
Temperature	180(1) K	150(1) K	150(1) K	150(1) K
Wavelength	1.54184 Å	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	P□2_1c	P□2_1c	P□2_1c	P□2_1c
Unit cell dimensions	a = 17.7047(2) Å	a = 17.5805(2) Å	a = 17.4530(2) Å	a = 17.7509(2)Å
	b = 17.7047(2) Å	b = 17.5805(2) Å	b = 17.4530(2) Å	b = 17.7509(2)Å
	c = 16.4257(2) Å	c = 16.5113(2) Å	c = 16.6568(2) Å	c = 16.2759(2) Å
	α= 90°	α= 90°	α= 90°	α= 90°
	β= 90°	β= 90°	β= 90°	β= 90°
	γ = 90°	γ = 90°	γ = 90°	γ = 90°
Volume	5148.74(9) Å^3	5103.21(7) Å^3	5073.78(7) Å^3	5128.45(9) Å^3
Z	2	2	2	2
Density (calculated)	1.909 gcm^{-3}	1.930 gcm^{-3}	1.977 g cm^{-3}	1.766 gcm^{-3}
Absorption coefficient	18.497 mm^{-1}	15.480 mm^{-1}	17.634 mm^{-1}	5.060 mm^{-1}
F(000)	2896	2904	2956	2740
Crystal size (max x mid x min)	0.255 x 0.201 x 0.05 mm^3	0.17 x 0.16 x 0.16 mm^3	0.18 x 0.15 x 0.11 mm^3	0.439 x 0.242 x 0.106 mm^3
Theta range for data collection	7.06 to 153.522°	7.11 to 134.054°	7.162 to 134.158°	7.042 to 134.158°
Index ranges	-21<=h<=22 -22<=k<=20 -20<=l<=20	-21<=h<=21 -19<=k<=21 -19<=l<=16	-19<=h<=20 -20<=k<=20 -19<=l<=18	-21<=h<=20 -21<=k<=21 -19<=l<=19
Reflections collected	35749	35230	36897	35166
Independent reflections	5354 R(int) = 0.0487	4546 R(int) = 0.0262	4526 R(int) = 0.0316	4579 R(int) = 0.0234
Completeness to theta	99.9 %	100 %	100 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5354 / 42 / 343	4546 / 18 / 331	4526 / 82 / 369	4579 / 3 / 343
Goodness-of-fit on F2	1.041	1.039	1.070	1.067
Final R indices [I>2sigma(I)]	R_1 = 0.0439 wR_2 = 0.1126	R_1 = 0.0320 wR_2 = 0.0829	R_1 = 0.0239 wR_2 = 0.0656	R_1 = 0.0215 wR_2 = 0.0594
R indices (all data)	R_1[a] = 0.0456 wR_2[b] = 0.1142	R_1 = 0.0322 wR_2 = 0.0830	R_1 = 0.0243 wR_2 = 0.0658	R_1 = 0.0217 wR_2 = 0.0595
Extinction coefficient	n/a	n/a	n/a	n/a
Largest diff. peak and hole	0.88 and -0.92 e.Å^{-3}	0.67 and -0.85 e.Å^{-3}	0.58 and -0.62 e.Å^{-3}	0.36 and -0.51 e.Å^{-3}

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + [(ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table S2. Shape measures of the 8-coordinate M1 (M = Gd, Tb, Dy, Y) coordination polyhedra in **1**·3MeCN, **2**·3MeCN, **3**·4MeCN and **4**·4MeCN, respectively.

Complex	**1**·3MeCN	**2**·3MeCN	**3**·4MeCN	**4**·4MeCN
Polyhedron[a]	Gd1	Tb1	Dy1	Y1
OP-8	34.73	35.06	35.06	34.88
HPY-8	21.75	21.67	21.81	22.07
HBPY-8	15.22	15.46	15.85	15.45
CU-8	11.50	11.81	12.30	11.97
SAPR-8	4.83	4.77	4.85	4.69
TDD-8	**2.87**	**2.73**	**2.61**	**2.57**
JGBF-8	12.54	12.59	12.65	12.39
JETBPY-8	26.85	26.96	27.31	27.12
JBTPR-8	4.57	4.52	4.54	4.27
BTPR-8	3.94	3.89	3.93	3.67
JSD-8	4.64	4.52	4.43	4.28
TT-8	12.28	12.59	13.06	12.71
ETBPY-8	23.19	23.15	23.44	23.46

[a] Abbreviations: OP-8, octagon; HPY-8, heptagonal pyramid; HBPY-8, hexagonal bipyramid; CU-8, cube; SAPR-8, square antiprism; TDD-8, triangular dodecahedron; JGBF-8, Johnson gyrobifastigium; JETBPY-8, Johnson elongated triangular bipyramid; JBTPR-8, Johnson biaugmented trigonal prism; BTPR-8, biaugmented trigonal prism; JSD-8, Johnson snub diphenoid; TT-8, triakis tetrahedron; ETBPY-8, elongated trigonal bipyramid. The values in boldface indicate the closest polyhedron according to the Continuous Shape Measures.

Table S3. Bond valence sum (BVS) calculations for O atoms of **1**·3MeCN, **2**·3MeCN, **3**·4MeCN and **4**·4MeCN, respectively, along with the assignment of the corresponding groups.[1]

	1·3MeCN	**2**·3MeCN	**3**·4MeCN	**4**·4MeCN	**Assignment**
O1	2.08	2.05	2.05	2.05	$(\mu\text{-OR})^-$
O2	1.88	1.89	1.89	1.89	$(\mu\text{-OR})^-$
O3	1.90	1.89	1.92	1.94	$(\mu\text{-OR})^-$
O4	1.88	1.86	1.86	1.85	$(\mu\text{-OR})^-$
O5	1.04	1.08	1.07	1.07	ROH

Table S4. Selected interatomic distances (Å) and angles (°) for **1**·3MeCN, **2**·3MeCN, **3**·4MeCN and **4**·4MeCN.

1·3MeCN			
Bond lengths			
Gd(1)-O(1)	2.260(6)	Cu(1)-O(1)	1.894(6)
Gd(1)-O(3)' [c]	2.273(6)	Cu(1)-O(2)	1.918(6)
Gd(1)-O(2)''' [a]	2.328(6)	Cu(1)-O(2)''' [a]	1.918(6)
Gd(1)-O(4)' [c]	2.319(6)	Cu(2)-O(3)	1.946(7)
Gd(1)-O(6)	2.481(7)	Cu(2)-O(4)	1.925(7)
Gd(1)-O(7)	2.498(8)	Cu(2)-N(1)	2.002(8)
Gd(1)-O(9)	2.484(9)	Cu(2)-N(2)	2.017(8)
Gd(1)-O(10)	2.522(9)	Cu(2)-O(5)	2.397(9)
Cu(1)-O(1)''' [a]	1.893(6)		
Bond angles			
Cu(1)-O(1)-Gd(1)	104.1(3)	Cu(1)-O(2)-Gd(1)''' [a]	100.8(2)
Cu(2)-O(3)-Gd(1)'' [b]	103.6(3)	Cu(2)-O(4)-Gd(1)'' [b]	102.6(3)
2·3MeCN			
Bond lengths			

Tb(1)-O(1)	2.244(5)	Cu(1)-O(1)’’’ [a]	1.888(5)
Tb(1)-O(3)’ [c]	2.259(5)	Cu(1)-O(2)	1.912(5)
Tb(1)-O(4)’ [c]	2.302(5)	Cu(1)-O(2)’’’ [a]	1.912(5)
Tb(1)-O(2)’’’ [a]	2.325(5)	Cu(2)-O(3)	1.935(6)
Tb(1)-O(6)	2.475(5)	Cu(2)-O(4)	1.925(6)
Tb(1)-O(7)	2.489(6)	Cu(2)-N(1)	2.004(6)
Tb(1)-O(9)	2.481(7)	Cu(2)-N(2)	2.007(6)
Tb(1)-O(10)	2.511(7)	Cu(2)-O(5)	2.417(7)
Cu(1)-O(1)	1.888(5)		
Bond angles			
Cu(1)-O(1)-Tb(1)	104.1(2)	Cu(1)-O(2)-Tb(1)’’’ [a]	100.4(2)
Cu(2)-O(3)-Tb(1)’’ [b]	103.8(2)	Cu(2)-O(4)-Tb(1)’’ [b]	102.6(2)
3·4MeCN			
Bond lengths			
Dy(1)-O(1)	2.227(4)	Cu(1)-O(1)’’’ [a]	1.887(4)
Dy(1)-O(3)’’ [b]	2.249(4)	Cu(1)-O(2)	1.916(4)
Dy(1)-O(2)’’’ [a]	2.302(4)	Cu(1)-O(2)’’’ [a]	1.916(4)
Dy(1)-O(9)	2.465(4)	Cu(2)-O(3)	1.937(4)
Dy(1)-O(4)’’ [b]	2.291(4)	Cu(2)-O(4)	1.933(4)
Dy(1)-O(10)	2.469(4)	Cu(2)-N(1)	1.999(5)
Dy(1)-O(7)	2.496(5)	Cu(2)-N(2)	1.997(5)
Dy(1)-O(6)	2.459(5)	Cu(2)-O(5)	2.452(6)
Cu(1)-O(1)	1.887(4)		
Bond angles			
Cu(1)-O(1)-Dy(1)	104.2(2)	Cu(1)-O(2)-Dy(1)’’’ [a]	100.5(2)
Cu(2)-O(3)-Dy(1)’ [c]	103.8(2)	Cu(2)-O(4)-Dy(1)’ [c]	102.4(2)
4·4MeCN			
Bond lengths			
Y(1)-O(1)	2.215(3)	Cu(1)-O(1)’’’ [a]	1.887(2)
Y(1)-O(2)’’’ [a]	2.297(3)	Cu(1)-O(2)	1.920(2)
Y(1)-O(3)’’ [b]	2.239(3)	Cu(1)-O(2)’’’ [a]	1.920(2)

Y(1)-O(4)'' [b]	2.290(3)	Cu(2)-O(3)	1.946(3)
Y(1)-O(9)	2.451(3)	Cu(2)-O(4)	1.933(3)
Y(1)-O(6)	2.439(3)	Cu(2)-N(1)	2.001(3)
Y(1)-O(10)	2.454(3)	Cu(2)-N(2)	2.009(3)
Y(1)-O(7)	2.490(3)	Cu(2)-O(5)	2.396(3)
Cu(1)-O(1)	1.887(2)		
Bond angles			
Cu(1)-O(1)-Y(1)	104.6(2)	Cu(2)-O(3)-Y(1)' [c]	103.4(2)
Cu(1)-O(2)-Y(1)''' [a]	100.5(2)	Cu(2)-O(4)-Y(1)' [c]	102.0(2)

[a] ''' = 1- x, 1-y, +z; [b] '' = 1-x, +y, 1-z; [c] ' = +x, 1-y, 1-z.

Table S5. Crystallographically characterized compounds containing the ligand 2-methyl-2-(2-pyridyl)-1,3-propane-diol.

Compound	Reference
$[Mn_3Na(L)_4(MeCO_2)(MeOH)_2](ClO_4)_2{\cdot}3H_2O$[a]	2
$[Mn_3Na(L)_4(MeCO_2)(MeOH)_2](ClO_4)_2{\cdot}2MeOH{\cdot}H_2O$[a]	2
$[Cu_3(LH)_4]Cl_2$[a]	3
$[Cu_3(LH)_4](CF_3SO_3)_2$[a]	3
$[Cu_2(LH)_2Cl_2]$[a]	3
$[Cu_2(LH)_2Cl_2(MeOH)_2]$[a]	3
$[Cu(LH_2)_2](CuCl_4)$[a]	3
$[Cu(LH_2)_2](CF_3SO_3)_2$[a]	3

[a] H_2L =2-methyl-2-(2-pyridyl)-1,3-propane-diol

Physical Measurements/Characterization

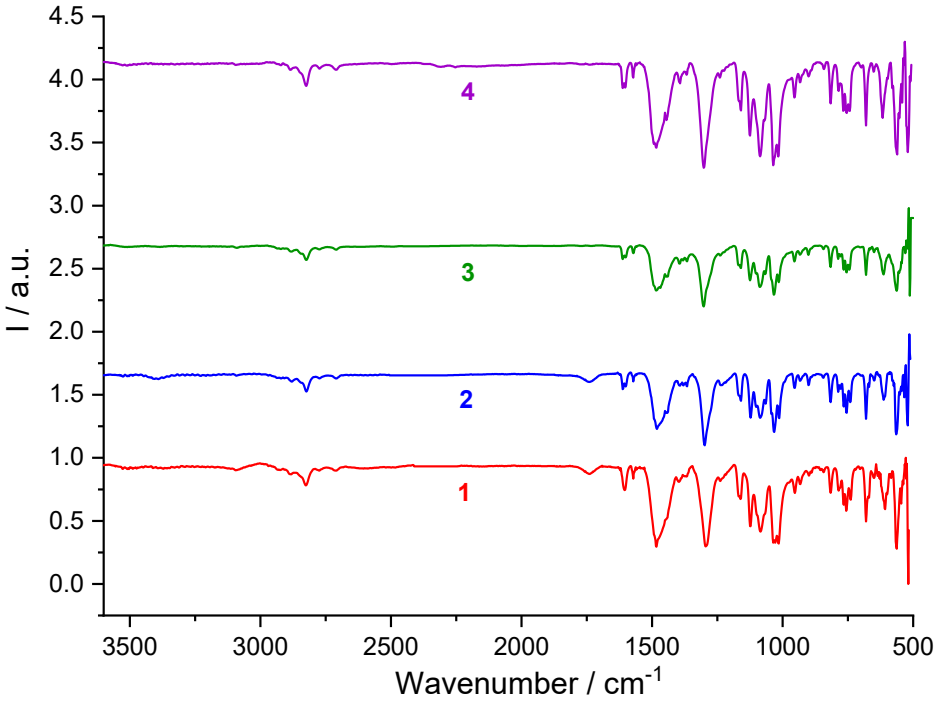

Figure S1. IR spectra of compounds **1** - **4**.

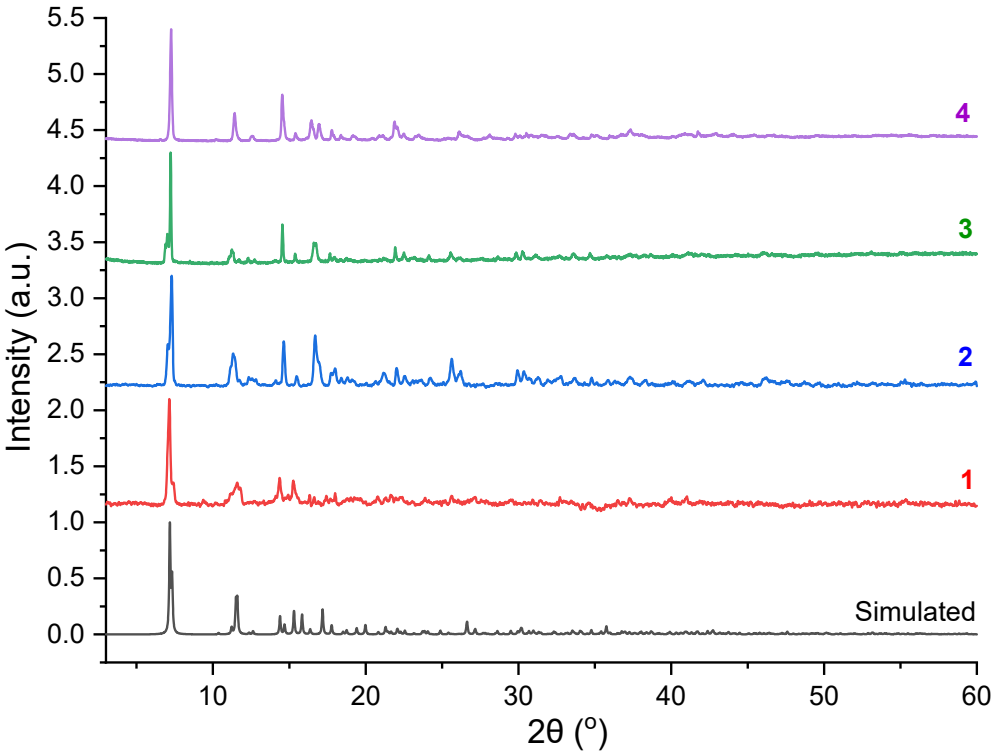

Figure S2. Powder X-ray diffraction patterns of compounds **1** - **4**, along with the simulated pattern from the single crystal data.

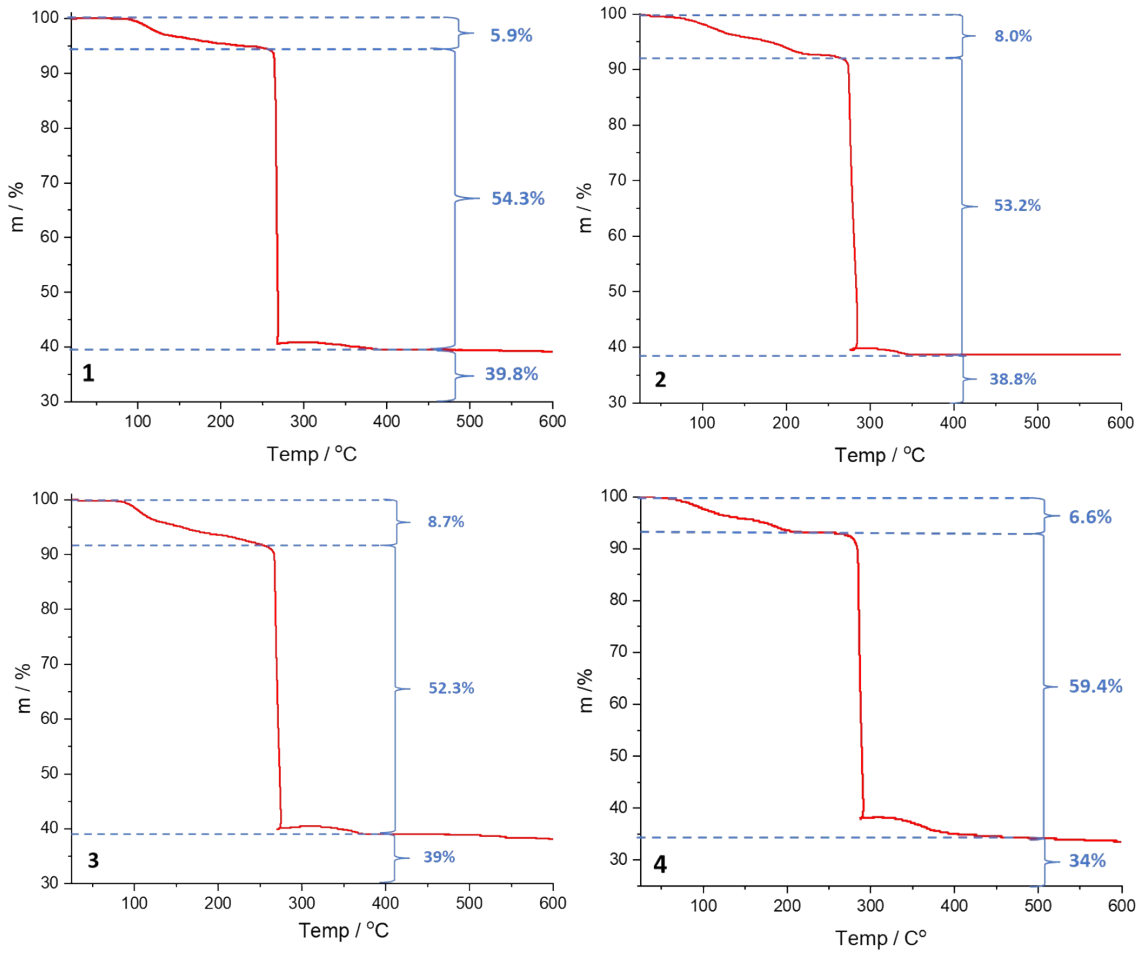

Figure S3. TGA graphs of compounds **1** - **4**.

Table S6. Calculated values for percentage mass loss of solvent removal and ligand combustion along with the experimental values obtained from TGA analysis of compounds **1** - **4**, respectively.

Removal of Lattice Solvents				Ligand Combustion		Residual Oxide(s)		
Compound	Temperature (°C)	Experimental (Calculated) (%)	xH_2O	Temperature (°C)	Experimental (Calculated) (%)	Temperature (°C)	Experimental (Calculated) (%)	Formula
1	r.t.-240	5.9 (6.0)	x=10	240-400	54.3 (54.1)	600	39.8 (39.9)	$6CuO/2Gd_2O_3$
2	r.t.-240	8.0 (8.1)	x=14	240-400	53.2 (52.3)	600	38.8 (39.6)	$6CuO/Tb_4O_7$
3	r.t.-240	8.7 (8.6)	x=15	240-400	52.3 (52.3)	600	39.0 (39.1)	$6CuO/2Dy_2O_3$
4	r.t.-240	6.6 (6.6)	x=10	240-400	59.4 (59.5)	600	34.0 (33.9)	$6CuO/2Y_2O_3$

Magnetic measurements

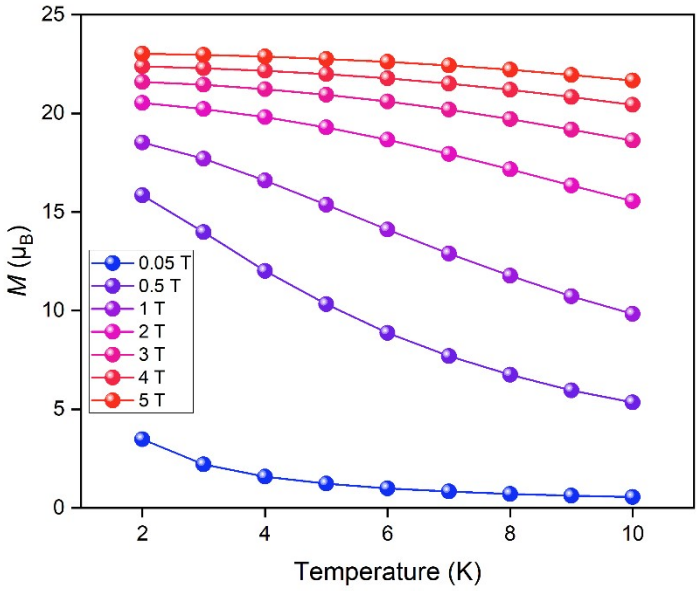

Figure S4. Magnetization (*M*) vs. temperature (*T*) plot for **2**.

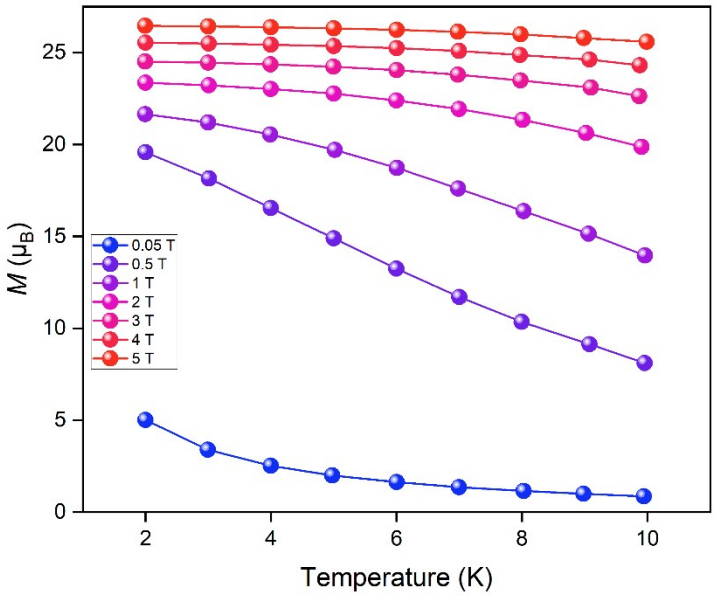

Figure S5. Magnetization (*M*) vs. temperature (*T*) plot for **3**.

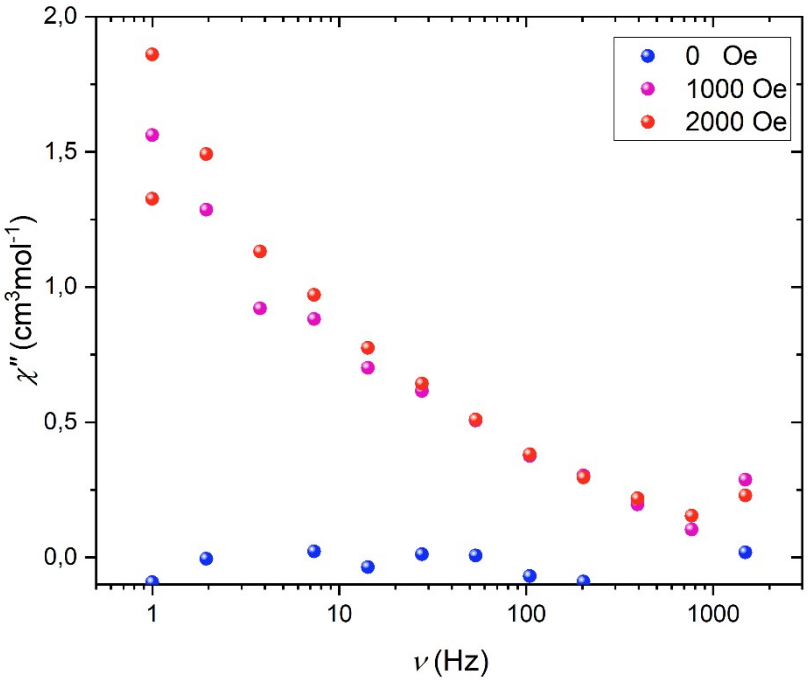

Figure S6. Plot of the out-of-phase (χ''_M) signal as χ''_M *vs.* ν in a 3.5 G ac field at the indicated applied dc fields for **1** at 2 K.

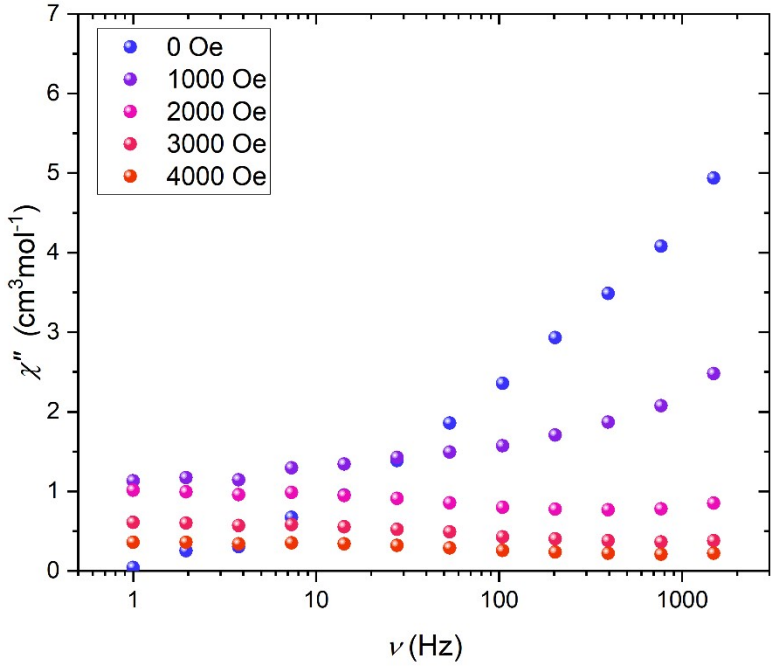

Figure S7. Plot of the out-of-phase (χ''_M) signal as χ''_M *vs.* ν in a 3.5 G ac field at the indicated applied dc fields for **2** at 2 K.

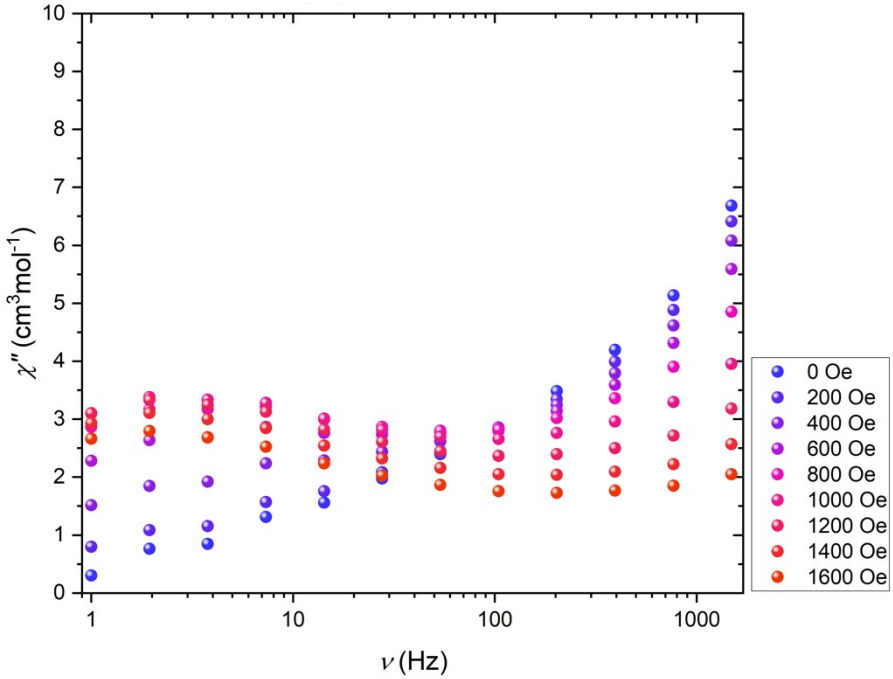

Figure S8. Plot of the out-of-phase (χ''_M) signal as χ''_M *vs.* ν in a 3.5 G ac field at the indicated applied dc fields for **3** at 2 K.

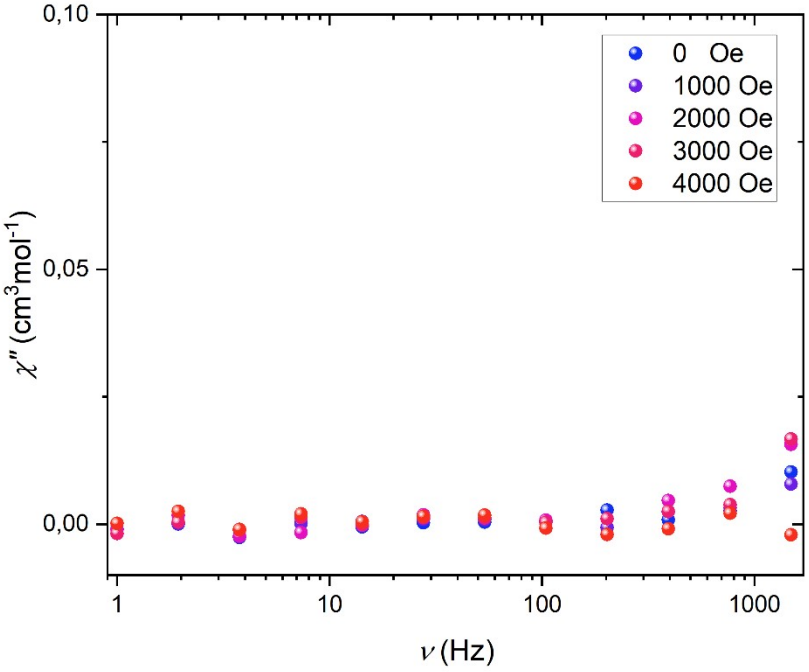

Figure S9. Plot of the out-of-phase (χ''_M) signal as χ''_M *vs.* ν in a 3.5 G ac field at the indicated applied dc fields for **4** at 2 K.

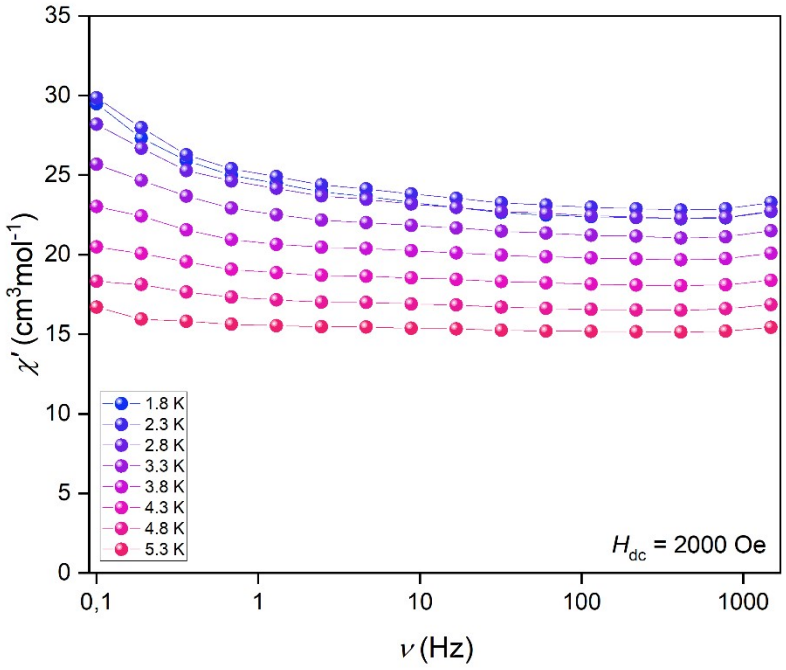

Figure S10. Plot of the in-phase (χ'_M) signal as χ'_M *vs.* ν, in the presence of a 0.2 T dc field, for **1**.

References

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