ELECTRONIC SUPPORTING INFORMATION

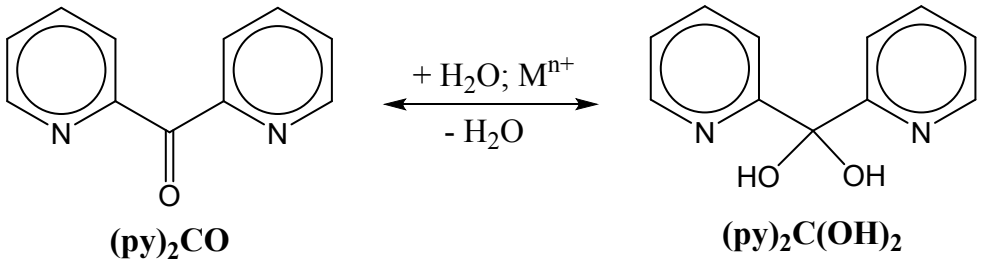
Heterometallic Cu/Ln cluster chemistry: Ferromagnetically-coupled $\{Cu_4Ln_2\}$ complexes exhibiting single-molecule magnetism and magnetocaloric properties

Dimitris I. Alexandropoulos,[a] Luis Cunha-Silva,[b] Jinkui Tang,[c] and Theocharis C. Stamatatos*[a]

[a] *Department of Chemistry, 1812 Sir Isaac Brock Way, Brock University, L2S 3A1 St. Catharines, Ontario, Canada. E-mail: tstamatatos@brocku.ca; Tel: (+1)-905-688-5550 Ext. 3400*

[b] *REQUIMTE-LAQV & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal*

[c] *State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China*



Scheme S1. Structural formulae and abbreviations of the ligands discussed in the text.

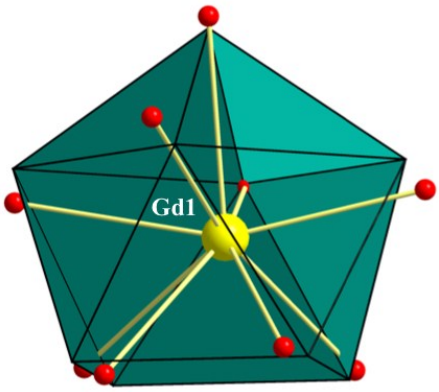


Figure S1. Spherical capped square antiprismatic coordination geometry of the Gd^{3+} ions in **1**. Points connected by the black thin lines define the vertices of the ideal polyhedron.

Table S1. SHAPE measures of the 9-coordinate lanthanide coordination polyhedra.

Polyhedron[a,b]	Gd1	Tb1	Dy1
EP-9	36.18	36.22	36.40
OPY-9	21.25	21.21	21.23
HBPY-9	17.77	17.96	17.87
JTC-9	14.93	15.00	14.99
JCCU-9	9.16	9.18	9.15
CCU-9	8.06	8.10	8.07
JCSAPR-9	3.50	3.41	3.31
CSAPR-9	**2.48**	**2.46**	**2.29**

JTCTPR-9	4.55	4.42	4.29
TCTPR-9	2.74	2.61	2.50
JTDIC-9	10.69	10.53	10.58
HH-9	10.85	10.87	10.92
MFF-9	2.84	2.82	2.68

[a] Abbreviations: EP-9, enneagon; OPY-9, octagonal pyramid; HBPY-9, Heptagonal bipyramid; JTC-9, Johnson triangular cupola J3; JCCU-9, capped cube J8; CCU-9, spherical-relaxed capped cube; JCSAPR-9, capped square antiprism J10; CSAPR-9, spherical capped square antiprism; JTCTPR-9, tricapped trigonal prism J51; TCTPR-9, spherical tricapped trigonal prism; JTDIC-9, tridiminished icosahedron J63; HH-9, hula-hoop; MFF-9, muffin.

[b] The values in boldface indicate the closest polyhedron according to the Continuous Shape Measures.

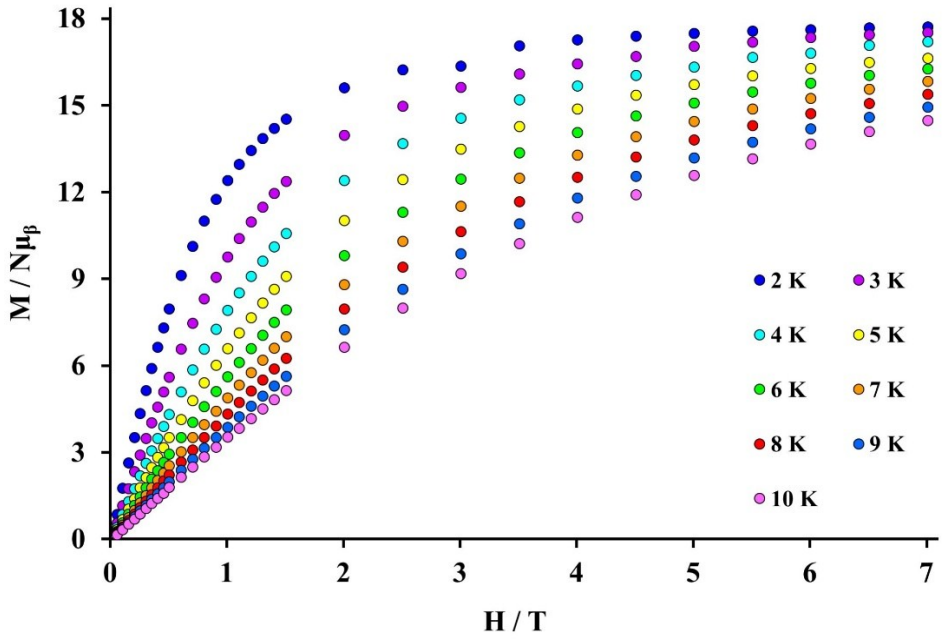


Figure S2. Isothermal magnetization (*M*) curves for complex **1** in the 2 to 10 K range.

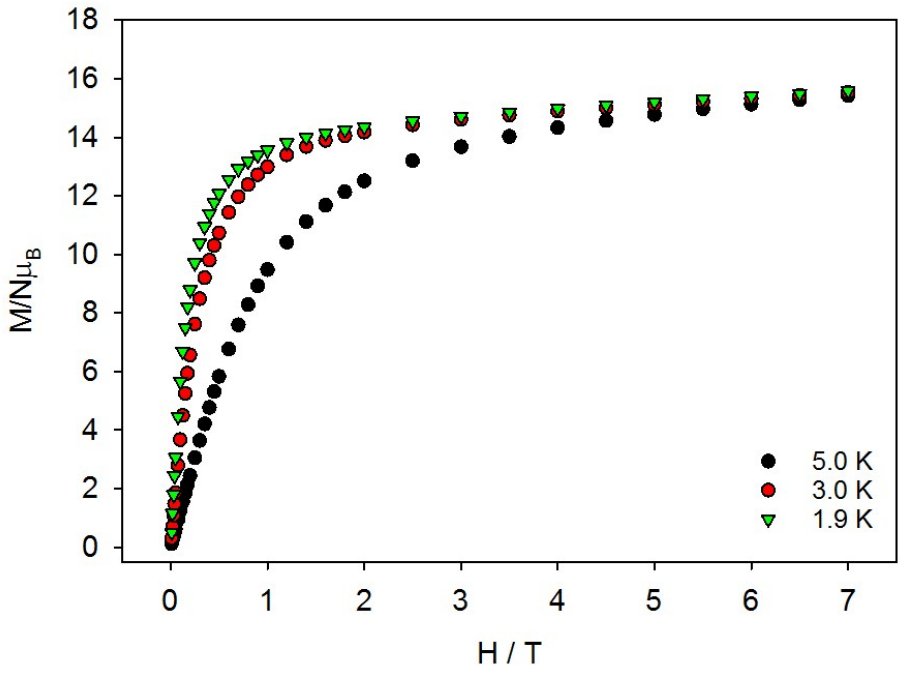


Figure S3. Magnetization (*M*) vs field (*H*) plots for complex **2** at various low temperatures.

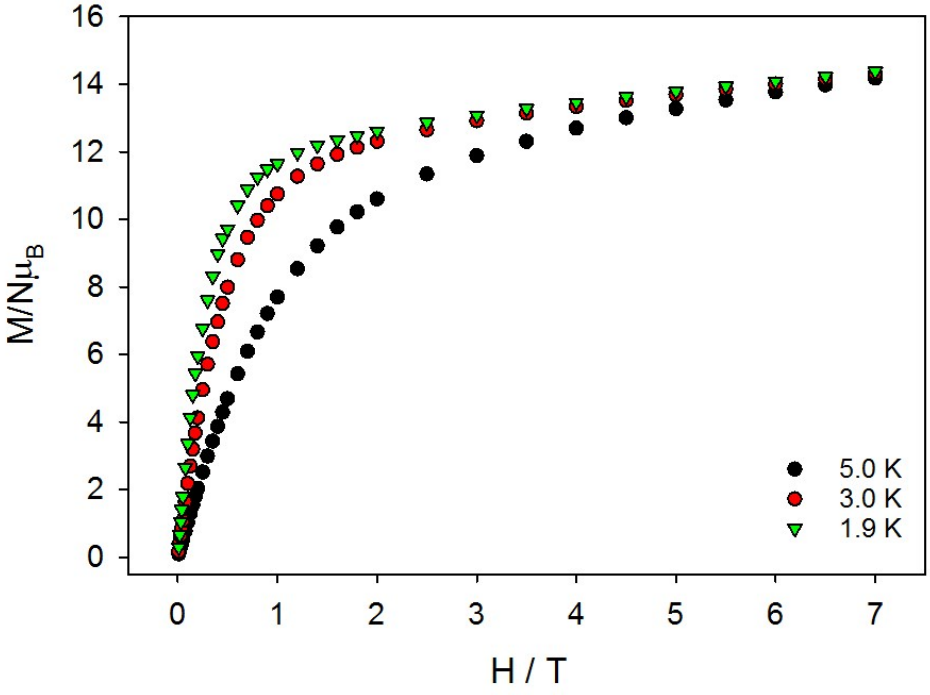


Figure S4. Magnetization (*M*) vs field (*H*) plots for complex **3** at various low temperatures.

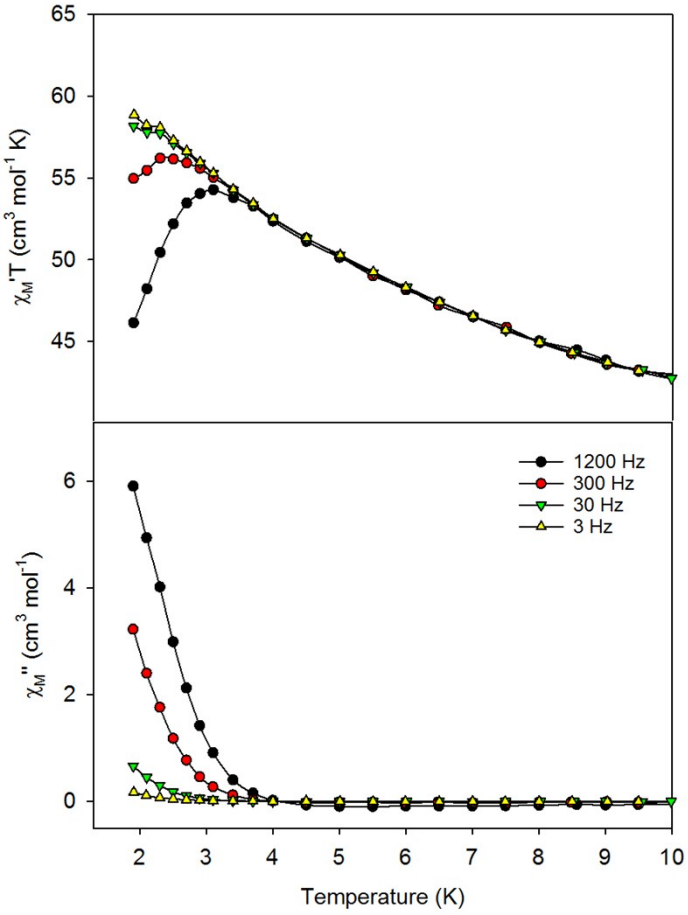


Figure S5. Temperature dependence of the in-phase $\chi_M'T$ product (top) and out-of-phase χ_M'' (bottom) *ac* susceptibility signals of **2** in a 3.0 G field oscillating at the indicated frequencies.

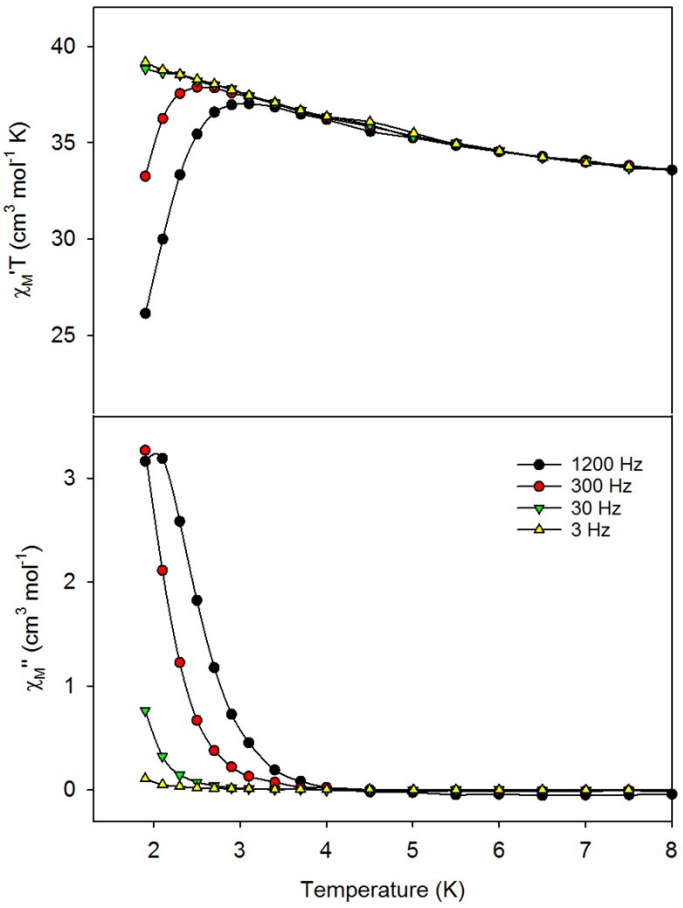


Figure S6. Temperature dependence of the in-phase $\chi_M'T$ product (top) and out-of-phase χ_M'' (bottom) *ac* susceptibility signals of **3** in a 3.0 G field oscillating at the indicated frequencies.