

Supporting information for

Co₃Gd₄ cage as magnetic refrigerant and Co₃Dy₃ cage showing slow relaxation of magnetisation

Javeed Ahmad Sheikh*, Himanshu Sekhar Jena and Sanjit Konar

Experimental Section

X-ray Crystallography

Synthesis

[Co₃Gd₄(μ₃-OH)₂(CO₃)(O₂C^tBu)₁₁(teaH)₃]·5H₂O (1)

[Co₂(μ-OH₂)(O₂C^tBu)₄](HO₂C^tBu)₄, Co₂ (100mg, 0.1mmol) was dissolved in CH₃CN (8mL) and triethanolamine, teaH₃ (22mg, 0.15mmol) was added to the solution while stirring followed by the addition of Gd(NO₃)₃·6H₂O (45 mg, 0.1mmol) and final mixture was further stirred for ~12 hrs at room temperature. The solution was filtered and the filtrate was kept at 4^oC for slow evaporation. Within 3-4 days purple block shaped single crystals suitable for X-ray analysis were formed. The crystals were collected by filtration, washed with cold CH₃CN and dried in air. Yield, 43% based on Co₂. Elemental analysis: Calcd.(found) for C₇₄H₁₃₆Co₃Gd₄N₃O₄₄: C, 34.48(34.51); H, 5.31(5.34); N, 1.63(1.67). Selected IR data (KBr pellet): 3404 (b), 2952 (s), 1607 (s), 1474 (s), 1412 (m), 1374 (w), 1217 (s), 1123.5 (w), 883 (w), 572 (b) cm⁻¹.

[Co₃Dy₃(μ₃-OH)₄(O₂C^tBu)₆(teaH)₃](NO₃)₂·H₂O (2)

1	2
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The same procedure as that of **1** was used for the synthesis of this compound except that Dy(NO₃)₃·6H₂O (45 mg, 0.1mmol) was added instead of Gd(NO₃)₃·6H₂O. Yield, 47% based on Co₂. Elemental analysis: Calcd.(found) for C₄₈H₈₈Co₃Dy₃N₅O₃₅: C, 29.42(29.45); H, 4.52(4.54); N, 3.57(3.59). Selected IR data (KBr pellet): 3438.7 (b), 2961.7 (s), 2075.2 (b), 1560.3 (w), 1484 (s), 1410.5 (m), 1227.9 (s), 1103.5 (m), 923.9 (w), 558.7 (b) cm⁻¹.

Co site	BVS (Assigned oxidation state)	Co site	BVS (Assigned oxidation state)
Co1	2.86(3)	Co1	2.86(3)
Co2	2.83(3)	Co2	2.83(3)
Co3	2.88(3)	Co3	2.82(3)

Table S1. BVS calculations for complexes **1** and **2**.

Table S2. Crystal Data and Structure Refinement for Complexes **1** and **2**

	1	2
Formula	C ₇₄ H ₁₃₆ Co ₃ Gd ₄ N ₃ O ₄₄	C ₄₈ H ₈₈ Co ₃ Dy ₃ N ₅ O ₃₅
Formula weight	2574.05	1951.50
T (K)	110(2)	110(2)
Wavelength (Å)	0.71073	0.71073
Space group	<i>P</i> -1	<i>P</i> 21/ <i>c</i>
Crystal system	Triclinic	Monoclinic
<i>a</i> /Å	15.552(5)	30.554(17)
<i>b</i> /Å	16.373(6)	19.234(10)
<i>c</i> /Å	25.100(9)	30.327(17)
α /deg	77.745(2)	90.00
β /deg	89.127(2)	115.544(2)
γ /deg	65.270(2)	90.00
<i>V</i> /Å ³	5653(3)	16080(4)
<i>Z</i>	2	4
<i>D</i> _{calcd} (g cm ⁻³)	1.512	1.612
μ (mm ⁻¹)	2.818	3.435
<i>F</i> (000)	2576	7728
θ_{\min} , θ_{\max} (deg)	2.67, 25.00	2.19, 25.00
Reflection collected	19227	28319
unique reflections	19911	26869
R ₁ , wR ₂ (<i>I</i> ≥ 2σ(<i>I</i>))	0.0433, 0.1273	0.0760, 0.2181
Goodness of fit (GOF) on <i>F</i> ²	0.902	0.927

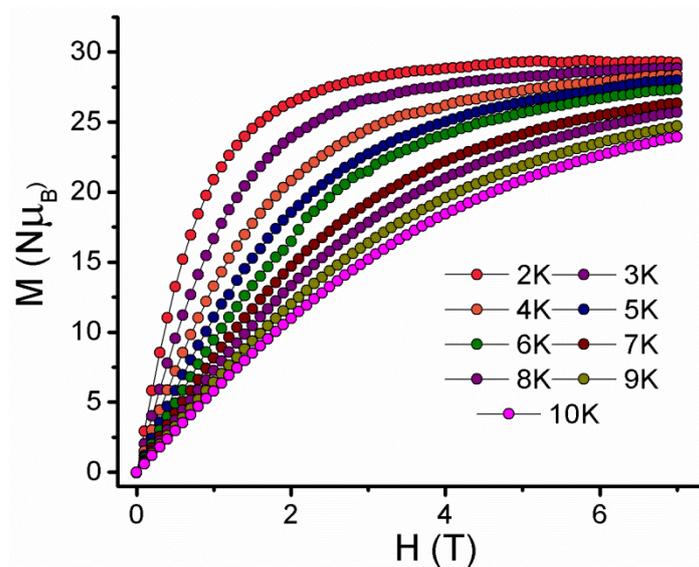


Figure S1 Field-dependencies of isothermal normalized magnetizations for complex **1** collected for temperatures ranging from 2-10 K

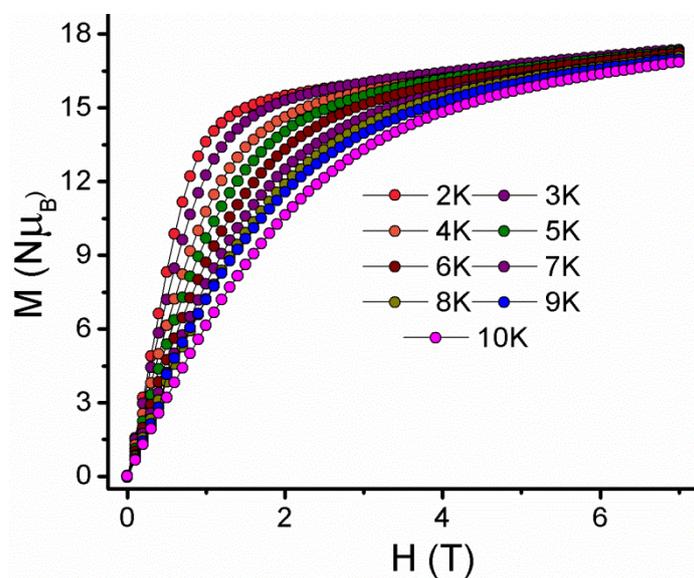


Figure S2 Field-dependencies of isothermal normalized magnetizations for complex **2** collected for temperatures ranging from 2-10 K.

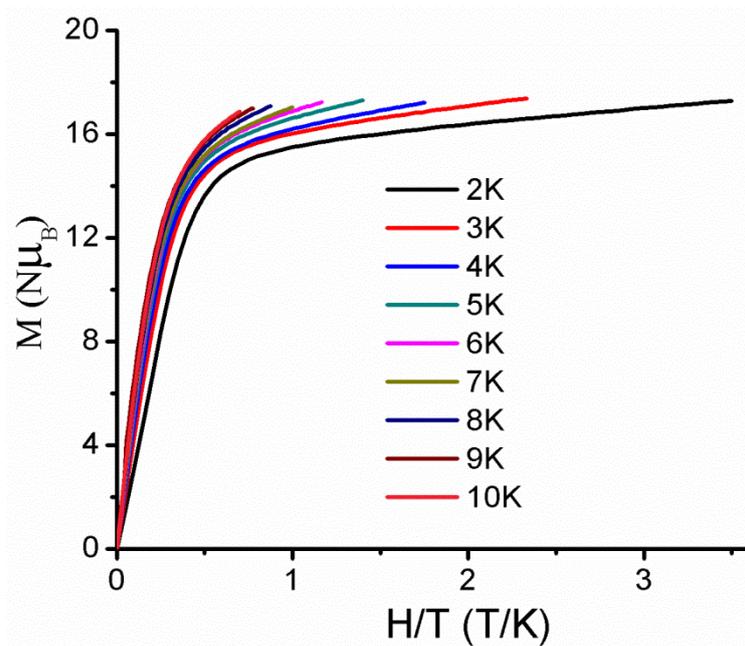


Figure S3 $M/N\mu_B$ vs H/T plots for complex 2 at 2-10 K.

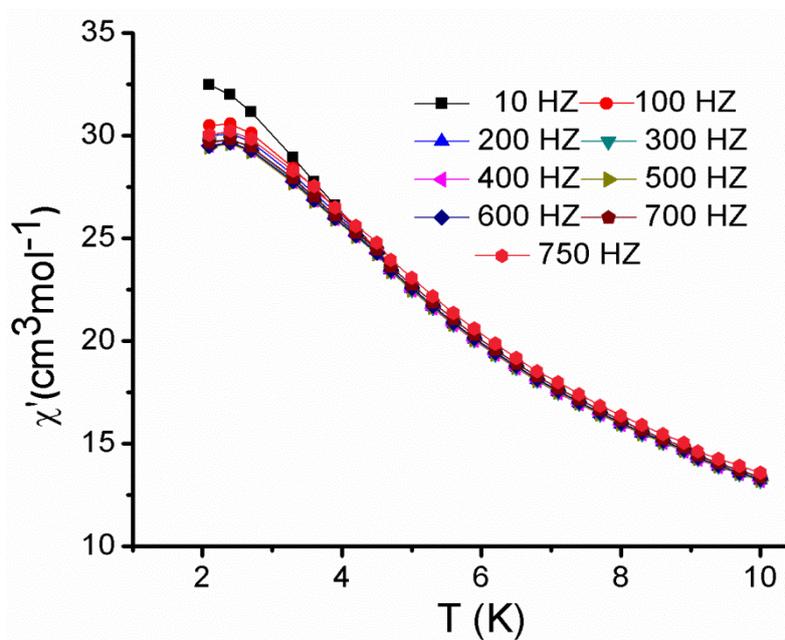


Figure S4 Temperature dependence of the in-phase (χ') ac susceptibility for complex 2 under zero dc field.

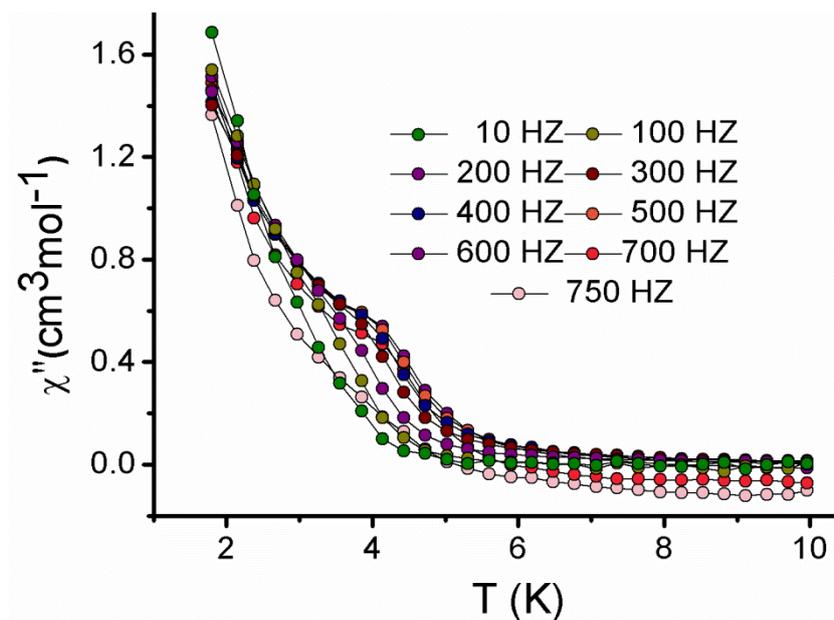


Figure S5 Temperature dependence of the out of phase (χ'') ac susceptibility for complex **2** under zero dc field.

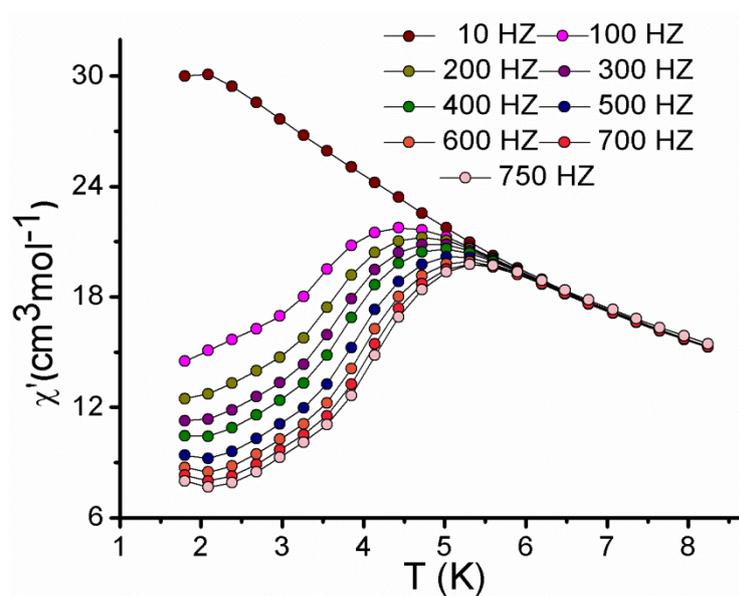


Figure S6 Temperature dependence of the in-phase (χ') ac susceptibility for complex **2** under 2000 Oe dc field.

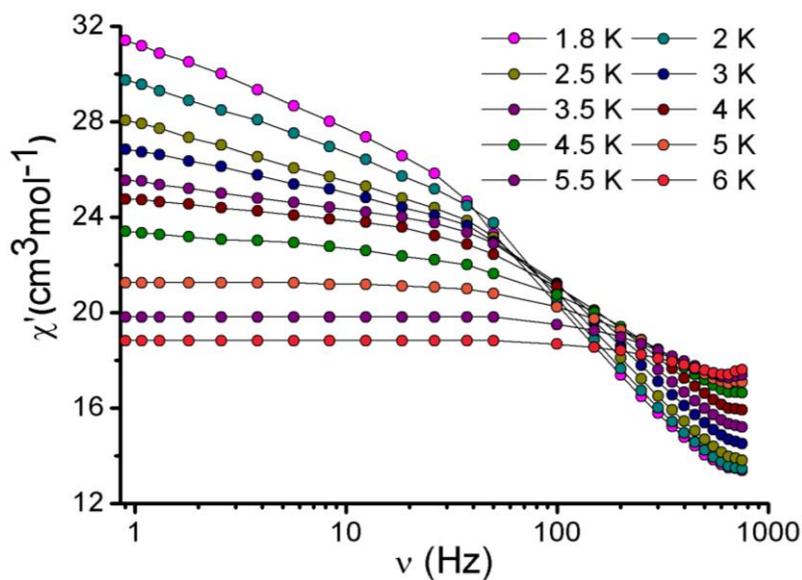


Figure S7 Frequency dependence of the in-phase (χ') ac susceptibility for complex **2** under 2000 Oe dc field.

References:

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