SUPPORTING INFORMATION

Molecular Nanoscale Magnetic Refrigerants: A Ferrimagnetic {Cu$^{II}_{15}$Gd$^{III}_{7}$} Cage-like Cluster from the Use of Pyridine-2,6-dimethanol

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Experimental Section

Syntheses. All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. $Cu(O_2CPh)_2 \cdot 2H_2O$ was prepared as a blue microcrystalline solid in high yield (~95%) by the 1:2 reaction of $CuSO_4 \cdot 5H_2O$ and NaO_2CPh in H_2O.

$[Cu_{15}Gd_7(OH)_6(CO_3)_4(O_2CPh)_{19}(pdm)_9(pdmH_2)_3(H_2O)_2]$ (1). To a stirred, pale yellow solution of $pdmH_2$ (0.14 g, 1.0 mmol) and NEt_3 (0.14 mL, 1.0 mmol) in MeCN (30 mL) were added solids $Gd(NO_3)_2 \cdot 6H_2O$ (0.45 g, 1.0 mmol) and $Cu(O_2CPh)_2 \cdot 2H_2O$ (0.34 g, 1.0 mmol) at the same time. The resulting, blue-colored, suspension was stirred for a further 45 min, filtered, and the filtrate was allowed to slowly evaporate at room temperature. After 10 days, X-ray quality blue crystals of **1**·4.5MeCN·1.5H$_2$O were collected by filtration, washed with cold MeCN (2 x 3 mL), and dried under vacuum; the yield was 20%. CCDC deposition number: 952810. Selected IR data (cm^{-1}) for **1**: 3422 (mb), 3062 (m), 2922 (m), 2842 (w), 1600 (s), 1558 (vs), 1470 (w), 1444 (m), 1398 (vs), 1266 (w), 1160 (m), 1064 (m), 847 (m), 830 (m), 782 (m), 722 (s), 676 (m), 562 (w), 500 (m), 438 (w).

Table S1. Bond Valence Sum Calculations[1] for Selected Oxygen Atoms in **1**[a]

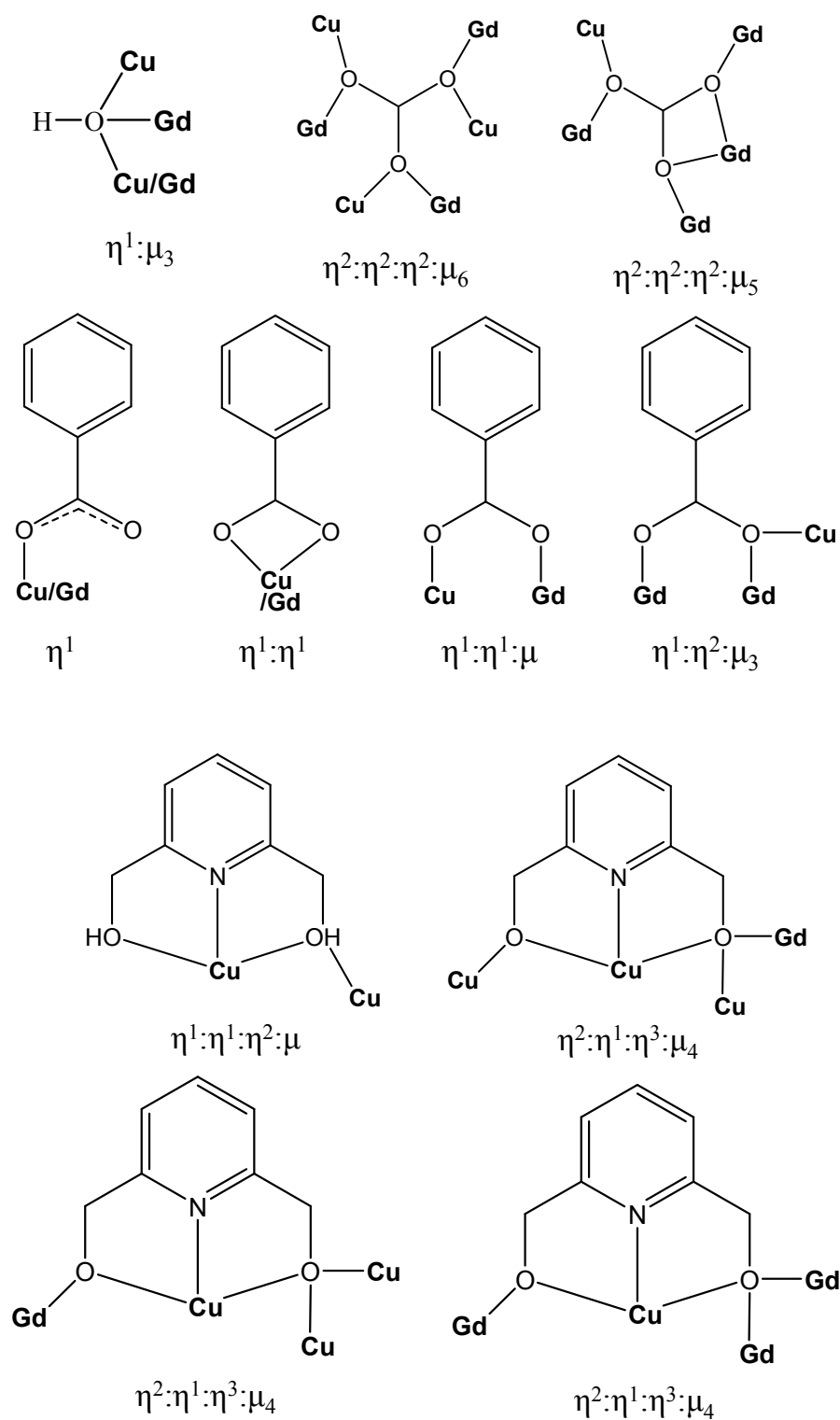|	BVS	assignment	group
O21	1.01	OH$^-$	
O22	1.23	OH$^-$	
O3	1.04	ROH	pdmH$_2$
O4	1.15	ROH	pdmH$_2$
O1W	0.26	H$_2$O	

[a] A BVS in the ~1.8-2.0, ~1.0-1.2, and ~0.2-0.4 ranges for an O atom is indicative of non-, single- and double-protonation, respectively, but can be altered somewhat by hydrogen bonding.

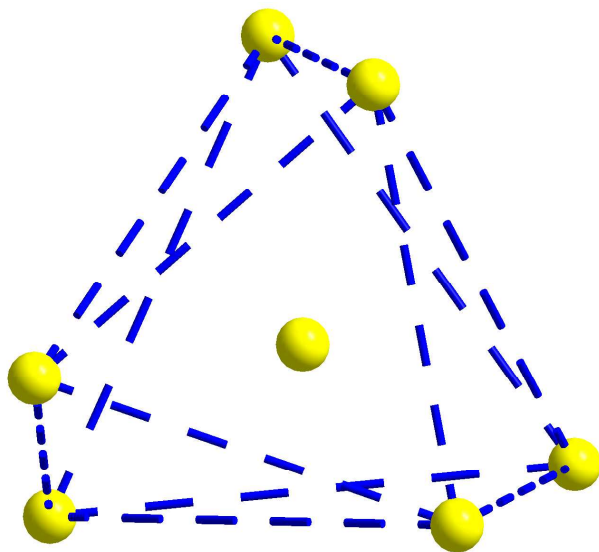[1] Brown, I. D.; Altermatt, D. *Acta Crystallogr. Sect. B* **1985**, 244.
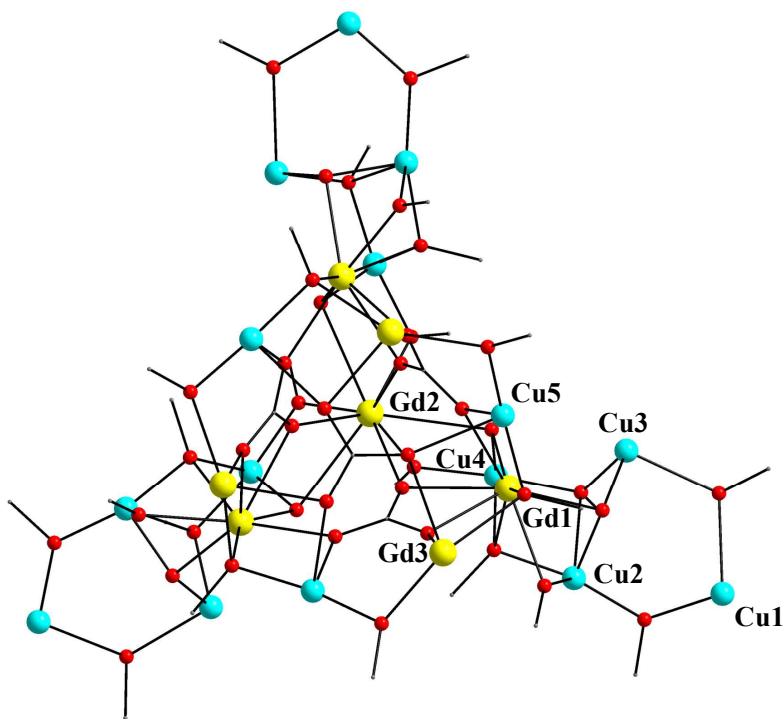
**Figure S1.** The complete $[Cu_{15}Gd_7(\mu_6\text{-}CO_3)(\mu_5\text{-}CO_3)_3(\mu_3\text{-}OH)_6(\mu_3\text{-}OR)_9(\mu\text{-}OR)_{15}]^{13+}$ core of **1**. Color scheme: Cu^{II} cyan, Gd^{III} yellow, O red, C gray.

$\eta^1:\mu_3$

$\eta^2:\eta^2:\eta^2:\mu_6$

$\eta^2:\eta^2:\eta^2:\mu_5$

η^1

$\eta^1:\eta^1$

$\eta^1:\eta^1:\mu$

$\eta^1:\eta^2:\mu_3$

$\eta^1:\eta^1:\eta^2:\mu$

$\eta^2:\eta^1:\eta^3:\mu_4$

$\eta^2:\eta^1:\eta^3:\mu_4$

$\eta^2:\eta^1:\eta^3:\mu_4$

Figure S2. The crystallographically established coordination modes of all ligands present in complex **1**.

Figure S3. The capped triangular antiprismatic topology of the Gd$_7$ subunit of **1**; the blue dashed lines indicate the Gd^{3+}…Gd^{3+} vectors in the triangular antiprism.
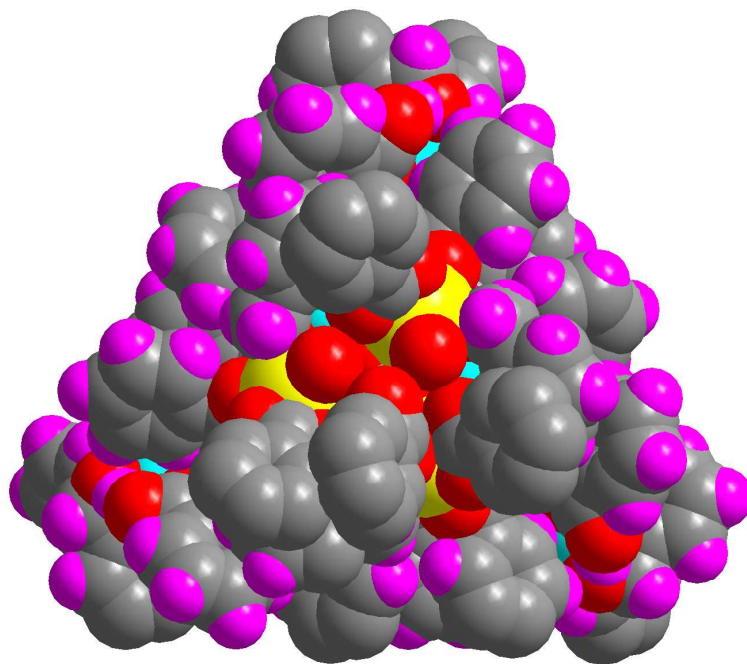
Figure S4. Space-filling representation of **1**. Color scheme: Cu^{II} cyan; Gd^{III} yellow, O red, N green, C gray, H purple.
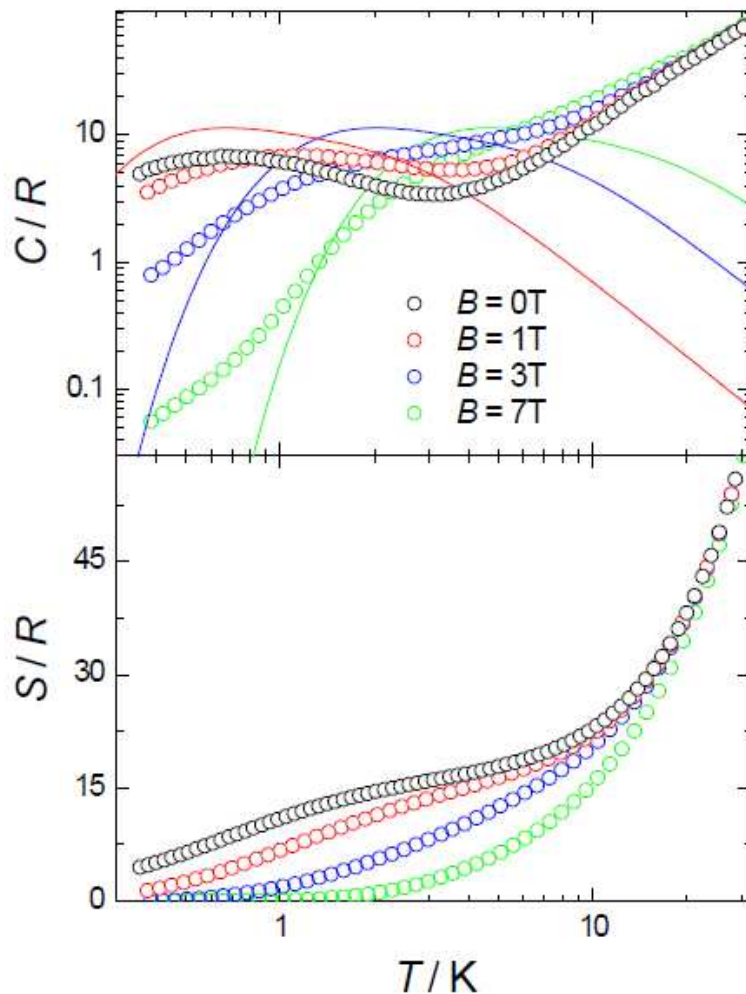
Figure S5. (top) Temperature dependencies of the heat capacity (*C*) of **1** normalized to the gas constant *R* collected for *B* = 0, 1, 3, and 7 T. (bottom) Temperature dependencies of the experimental magnetic entropy for several *B*, as obtained from the respective *C* data. The solid lines are the calculated Schottky contributions to the total *C*, which are due to field splitting and are obtained as the sum on non-interacting spin centers. As can be seen, these contributions are largely exceeding the maximum values of the experimental magnetic *C*, denoting that the applied fields used are not sufficient to magnetically decouple the spin centers.