

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

Despina Dermitzaki,[†] Giulia Lorusso,[‡] Catherine P. Raptopoulou,[△] Vassilis Psycharis,[△] Albert Escuer,^{*,§} Marco Evangelisti,^{*,‡} Spyros P. Perlepes,^{*,†} and Theocharis C. Stamatatos^{*,#}

[†] Department of Chemistry, University of Patras, 265 04 Patras, Greece

[‡] Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Universidad de Zaragoza, Departamento de Física de la Materia Condensada, 50009 Zaragoza, Spain

[§] Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

[△] Institute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, Department of Materials Science, NCSR "Demokritos", 153 10 Aghia Paraskevi Attikis, Greece

[#] Department of Chemistry, Brock University, L2S 3A1 St. Catharines, Ontario, Canada

Supporting Information

ABSTRACT: The employment of pyridine-2,6-dimethanol in 3d/4f-metal cluster chemistry has afforded a new {Cu^{II}₁₅Gd^{III}₇} cage-like molecule with a beautiful structure built by fused triangular subunits; the compound exhibits an overall ferrimagnetic behavior with an appreciable ground state spin value and shows promise as a low-temperature magnetic refrigerant.

One of the most fascinating challenges in modern coordination chemistry is undoubtedly the combination of an aesthetically pleasing structure with an interesting physical property or occasionally with more than one properties within the same molecular species. Polynuclear homometallic 3d- and 4f-metal complexes, as well as heterometallic 3d/3d'- and 3d/4f-metal compounds, are clearly excellent candidates to satisfy such expectations.¹ This is due to the pronounced ability of these metal ions to form and stabilize high-nuclearity and structurally complicated metal-oxido/hydroxido inorganic cores surrounded in periphery by organic bridging/chelating ligands. The type and nature of the latter groups play a significant role in the self-assembly synthesis of new polynuclear compounds and the choice of a small, flexible and polydentate ligand (or ligand 'blend') seems to be an attractive route.

The selection of the metal ion(s) is also of great importance because it directs the interest regarding the potential applications. Polynuclear 3d/4f-metal complexes (or coordination clusters) have shown a remarkable ability to act either as single-molecule magnets (SMMs)², mainly when the f-block ions are highly anisotropic and possess a significant spin (i.e., Dy^{III}, Tb^{III}), or as magnetic refrigerants³ when the molecules are isotropic and high-spin, conditions which are fulfilled by the co-presence of, for instance, Gd^{III} and Cu^{II} metal ions.

Magnetic refrigeration is based on the magnetocaloric effect (MCE). MCE deals with the change of magnetic entropy upon application of a magnetic field and can be used for cooling purposes via adiabatic demagnetization.⁴ In the last six years, the systematic exploration of the MCE in isotropic molecular magnetic compounds has demonstrated enormous values, larger than those observed on lanthanide alloys and magnetic nanoparticles.^{3,4} Such observations open a new window in molecular chemistry and the potential applications that coordination compounds could find as low-temperature magnetic coolers.

The MCE is greatly enhanced in molecules containing isotropic magnetic ions with large total spin S .³ Taking this into account, Cu²⁺/Gd³⁺ complexes seem very good candidates for molecular refrigerants as the Gd³⁺ ion has an isotropic f^7 configuration and the Cu²⁺/Gd³⁺ magnetic interactions are generally ferromagnetic in nature, leading to ground states with increased and large spin multiplicity.⁵ Further, the Cu²⁺/Gd³⁺ magnetic exchange interactions are very weak, due to the very efficient shielding of the Gd³⁺ 4f orbitals by the fully occupied 5s and 5p orbitals,⁵ and this generates multiple low-lying excited and field-accessible states, each of which can contribute to the magnetic entropy of the system. Magnetic entropy is related to the spin by $S_m = R \ln(2S + 1)$, where R is the gas constant. To date, the clusters with the largest MCE are homometallic {Gd₂}^{6a} and {Gd₂₄}^{1b}, and heterometallic {Ni₁₂Gd₃₆}^{6b} and {Mo₄Gd₁₂}^{6c} complexes with $-\Delta S_m$ values of ~ 40 , 46.1, 36.3 and 35.3 J kg⁻¹ K⁻¹ respectively, for liquid-helium temperatures and $\Delta B_0 = 7$ T.

In simple words, to construct polynuclear metal complexes behaving as magnetic coolers we need a metal-ligand 'blend' which will guarantee the aggregation of the metal ions into a large nuclearity motif and will produce a ferro- or ferrimagnetic system with negligible anisotropy. Toward this end, we have decided to employ the tridentate (N,O,O) ligand pyridine-2,6-dimethanol (pdmH₂) in heterometallic Cu²⁺/Gd³⁺

carboxylate chemistry as a means of satisfying the above requirements. Thus, the reaction of $\text{Cu}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, pdmH_2 , and NEt_3 in a 1:1:1:1 molar ratio in MeCN led to a blue suspension, which upon filtration gave a pale blue filtrate. The latter was allowed to slowly evaporate at room temperature, yielding after ten days blue, plate-like crystals of $[\text{Cu}_{15}\text{Gd}_7(\text{OH})_6(\text{CO}_3)_4(\text{O}_2\text{CPh})_{10}(\text{pdm})_9(\text{pdmH}_2)_3(\text{H}_2\text{O})_2]$ (**1**) in 20% yield.⁷ The formula of **1** is based on metric parameters, charge balance considerations and bond valence sum (BVS) calculations on the O atoms. The CO_3^{2-} ions are presumably derived from the fixation of atmospheric CO_2 .⁸ The identification of the CO_3^{2-} ions (vs NO_3^-) in **1** was determined via careful consideration of the X-ray diffraction data and observation of carbonate-related IR absorption bands at ~ 1400 and 845 cm^{-1} .⁸ Although rare, the co-presence of fully-deprotonated and neutral forms of an alkoxide-based ligand, as the $\text{pdm}^{2-}/\text{pdmH}_2$ combination in **1**, is with precedence in 3d/4f-metal cluster chemistry.⁹

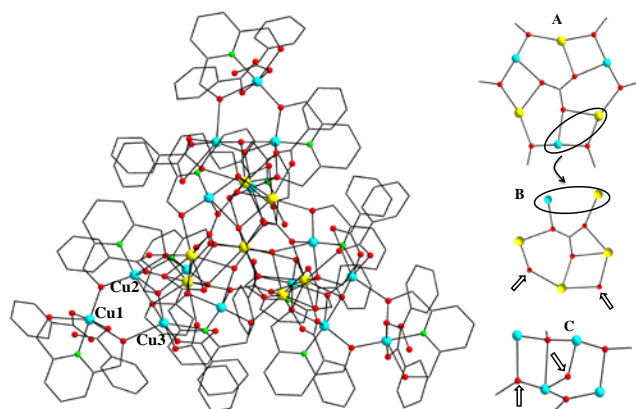


Figure 1. The structure of **1** (left) and the three different types of constituent subunits of its core (right). H-atoms are omitted for clarity. The circles and arrows indicate the connection ‘points’ between the subunits. Color scheme: Cu^{II} cyan; Gd^{III} yellow, O red, N green, C gray.

The structure of **1** consists of a $\{\text{Cu}^{II}_5\text{Gd}^{III}_7\}$ cage-like cluster (Figure 1, left) with a C_3 crystallographic symmetry (the 3-fold axis passing from the central, unique Gd₂ atom) and an irregular topology resulting from many fused triangular subunits. The metal ions within the core of **1** (Figure S1) are bridged by six $\mu_3\text{-OH}^-$, three $\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}\mu_3$ and an $\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}\mu_6$ CO_3^{2-} ions, and the alkoxido arms of nine $\eta^2\text{-}\eta^1\text{-}\eta^2\text{-}\mu_4$ pdm^{2-} and three $\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\mu$ pdmH_2 groups (Figure S2). Peripheral ligation about the core is provided by the chelating part of the $\text{pdm}^{2-}/\text{pdmH}_2$ groups, two terminal H_2O molecules, and nineteen PhCO_2^- ligands; the latter are arranged into four classes: seven are monodentate, with the dangling O atoms H-bonded to the OH-groups of the pdmH_2 ligands, six are bidentate-chelating, three are $\eta^1\text{-}\eta^1\text{-}\mu$ and three $\eta^1\text{-}\eta^1\text{-}\mu_3$. All Cu ions are six-coordinate with distorted octahedral geometries except Cu₄ and Cu₅ (and their symmetry-related partners) which are five-coordinate with almost perfect square pyramidal geometries ($\tau = 0.03$ and 0.06 , respectively). The Gd ions are nine- (Gd₁, Gd₂) and eight-coordinate (Gd₃) with very distorted geometries. The complicated core of **1** can be conveniently described as consisting of a central, non-planar, μ_6 -

carbonato-bridged $\{\text{Cu}_3\text{Gd}_3\}$ unit (**A**), each Cu...Gd edge of which being additionally linked to three Gd³⁺ ions by a $\mu_5\text{-CO}_3^{2-}$ (**B**). The resulting, inner $\{\text{Cu}_3\text{Gd}_7(\text{CO}_3)_4\}^{19+}$ subcore (**A+B**, Figure 1, right) is further bridged to three extrinsic $\{\text{Cu}_4\}$ subunits (**C**, Figure 1, right) through the μ_3 -hydroxido and alkoxido groups. Finally, regarding the topology of the seven Gd^{III} atoms, this could be roughly described as distorted, capped trigonal antiprismatic with Gd₂ occupying the capping site (Figure S3). The space-filling representation of **1** reveals its large nanometer-sized structure with an average diameter of ~ 2.6 nm as defined by the longest H...H distance (Figure S4). Complex **1** is the fourth largest Cu/Gd cluster isolated to date after the $\{\text{Cu}_{24}\text{Gd}_8\}^{10a}$, $\{\text{Cu}_{24}\text{Gd}_6\}^{10b}$ and $\{\text{Cu}_{36}\text{Gd}_{24}\}^{10c}$ cages, while it is one of the highest nuclearity heterometallic compounds^{10c} showing MCE (*vide infra*).

Solid-state direct current (dc) magnetic susceptibility (χ_M) data on dried **1**·2H₂O were collected in the 2.0–300 K range in applied fields of 0.3 T (300–30 K) and 0.02 T (30–2 K) to avoid saturation effects, and are plotted as $\chi_M T$ vs T in Figure 2. The $\chi_M T$ at 300 K is $66.79\text{ cm}^3\text{Kmol}^{-1}$, essentially equal to the calculated value of $66.98\text{ cm}^3\text{Kmol}^{-1}$ for fifteen Cu^{II} ($S = 1/2$) and seven Gd^{III} ($S = 7/2$, $L = 0$) non-interacting ions, assuming an average g value of 2.10. It slowly decreases with decreasing temperature to a value of $62.53\text{ cm}^3\text{Kmol}^{-1}$ at 20 K, and then rapidly increases to $79.93\text{ cm}^3\text{Kmol}^{-1}$ at 4.0 K before it drops to $64.78\text{ cm}^3\text{Kmol}^{-1}$ at 2.0 K. The shape of the $\chi_M T$ vs T plot indicates that both antiferro- and ferromagnetic exchange interactions dominate at different T regions, with the former roughly assigned to $\text{Cu}^{2+}\dots\text{Cu}^{2+}$ interactions and the latter to $\text{Cu}^{2+}\dots\text{Gd}^{3+}$ interactions. The ground state spin value of this ferrimagnetic system cannot be accurately determined due to its complicated structure with many fused triangular subunits. The magnetization measurements (inset of Figure 2) show a trend for saturation at a value of $58.3 N\mu_B$ at the highest fields and lowest temperatures employed, suggesting a net spin state of $S = 58/2 = 29$ for such fields. This can be tentatively rationalized assuming all the $\text{Cu}^{II}\dots\text{Gd}^{III}$ interactions to be ferromagnetic ($12 \times 1/2 + 7 \times 7/2 = 61/2$) and the interactions between the three extrinsic Cu^{II} ions (Cu₁, Cu_{1a}, Cu_{1b}) with their directly bridged Cu^{II} ions (Cu₂/Cu₃, Cu_{2a}/Cu_{3a}, Cu_{2b}/Cu_{3b}) to be antiferromagnetic, thus forcing those three $S = 1/2$ spins to align antiparallel to all other and resulting in a field-stabilized spin state of $S = 61/2 - 3/2 = 58/2$. This is likely to occur as the average Cu₁-O-Cu_{2/3} bond angle is $\sim 120^\circ$ which will be antiferromagnetic and stronger than the Cu₂-O-Cu₃ interaction (average angle of $\sim 101^\circ$).^{11a}

The large value for the magnetization makes **1** a possible candidate for low-temperature magnetic cooling and we have thus evaluated its MCE, which includes the calculation of the magnetic entropy change ΔS_m and adiabatic temperature change ΔT_{ad} for selected applied field changes ΔB_0 , from the measured heat capacity (Fig. S5) and magnetization (Fig. 2). As for the former, ΔS_m can be obtained from the T and field dependencies of the entropy. The results are shown in Figure 3. We report an appreciable value of $-\Delta S_m$ which reaches $\sim 22.2\text{ J kg}^{-1}\text{ K}^{-1}$ at $T = 2.5\text{ K}$ for $\Delta B_0 = 7\text{ T}$. This is what we could expect considering the large net magnetic moment and negligible anisotropy of the molecule, as well as the weak intra-cluster interactions involving Gd^{III} ions that lead to low-lying excited spin states.³ However, this value is still lower than

the maximum entropy value per mole ($25R \sim 33.5 \text{ J kg}^{-1} \text{ K}^{-1}$) for 15 Cu^{II} and 7 Gd^{III} fully decoupled ions. In the $2 \text{ K} < T < 6 \text{ K}$ range, the zero-field magnetic entropy shows a “plateau” at a considerably lower value, i.e., $\sim 17R$, indeed (Fig. S5). This is ascribed to the overall ferrimagnetism of **1** which results from the relatively strong antiferromagnetic $\text{Cu}^{\text{II}} \dots \text{Cu}^{\text{II}}$ exchange, and it is thus clear that this type of interaction is the least favorable for observing the maximum MCE.^{1b} Fields higher than 7 T are needed in order to fully break the antiferromagnetic exchanges (Fig. S5). In regards to the adiabatic temperature change, Figure 3 (bottom) shows that $\Delta B_0 = 7 \text{ T}$ provides a maximum $\Delta T_{\text{ad}} = 7.5 \text{ K}$ for the same temperatures at which we observe the $-\Delta S_{\text{m}}$ maxima. By lowering ΔB_0 to 3 and 1 T, ΔT_{ad} decreases to 4.2 and 1.7 K, respectively. Therefore, the field dependence of ΔT_{ad} increases slightly from nearly ~ 1 to $\sim 1.7 \text{ K T}^{-1}$, respectively, setting this material as a promising refrigerant for this low-temperature region.^{3,4,12}

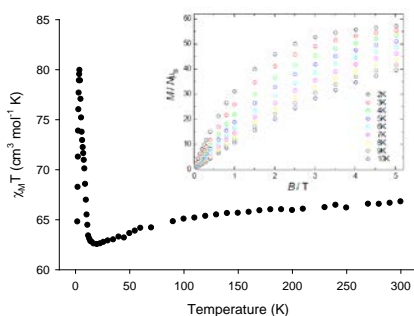


Figure 2. The $\chi_{\text{M}}T$ versus T plot of **1**. Inset: The field-dependent magnetization plot at indicated temperatures. Lines are guides to the eye.

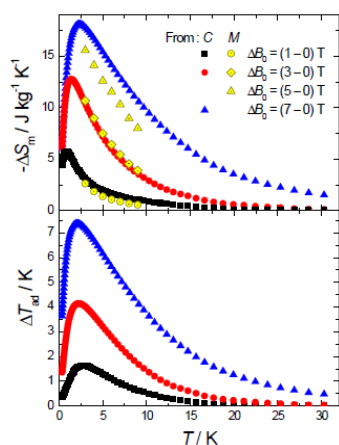


Figure 3. (top) T -dependencies of the magnetic entropy change as obtained from heat capacity (C) and magnetization (M) data, for the indicated applied field changes. (bottom) T -dependencies of the adiabatic temperature change obtained from C data, for the indicated applied field changes.

In conclusion, we have shown that the $\text{Cu}^{2+}/\text{Gd}^{3+}/\text{PhCO}_2^-/\text{pdmH}_2$ system is a promising reaction scheme to follow, not only for the synthesis of new, high-nuclearity heterometallic complexes with beautiful topologies, but also for magnetically interesting species with promising low- T MCE. We are currently focusing on the effect of the nature of the carbox-

ylate group on the $\{\text{Cu}_5\text{Gd}_7\}$ identity and the isolation of $\text{Cu}^{2+}/\text{Gd}^{3+}$ magnetic coolers with a larger MCE.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF format), synthetic details, and various structural and magnetism figures for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

* E-mail: tstamatatos@brocku.ca

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENTS

This work was supported by the CICYT (project CTQ2009-07264) and Excellence in Research ICREA-Academia Award (to A.E.), the MINECO (MAT2012-38318-Co3, to M.E. and G.L), an EU Marie Curie IEF (PIEF-GA-2011-299356, to G. L.), and the NSERC Discovery Grant (to Th.C.S.).

REFERENCES

- (1) (a) Zheng, Y.- Z.; Evangelisti, M.; Tuna, F.; Winpenney, R. E. P. *J. Am. Chem. Soc.* **2012**, *134*, 1057. (b) Chang, L.- X.; Xiong, G.; Wang, L.; Cheng, P.; Zhao, B. *Chem. Commun.* **2013**, 49, 1055.
- (2) Holyńska, M.; Premužić, Jeon, I.- R.; Wernsdorfer, W.; Clérac, R.; Dehnen, S. *Chem. Eur. J.* **2011**, *17*, 9605.
- (3) Evangelisti, M.; Brechin, E. K. *Dalton Trans.* **2010**, 39, 4672.
- (4) Evangelisti, M.; Luis, F.; de Jongh, L. J.; Affronte, M. *J. Mater. Chem.* **2006**, *16*, 2534.
- (5) Andruh, M.; Costes, J. P.; Diaz, C.; Gao, S. *Inorg. Chem.* **2009**, *48*, 3342.
- (6) (a) Evangelisti, M.; Roubeau, O.; Palacios, E.; Camón, A.; Hooper, T. N.; Brechin, E. K.; Alonso, J. *J. Angew. Chem. Int. Ed.* **2011**, *50*, 6606. (b) Peng, J.- B.; Zhang, Q.- C.; Kong, X.- J.; Ren, Y.- P.; Long, L.- S.; Huang, R.- B.; Zheng, L.- S.; Zheng, Z. *Angew. Chem. Int. Ed.* **2011**, *50*, 10649. (c) Zheng, Y.; Zhang, Q.- C.; Long, L.- S.; Huang, R.- B.; Müller, A.; Schnack, J.; Zheng, L.- S.; Zheng, Z. *Chem. Commun.* **2013**, 49, 36.
- (7) Anal. Calcd (Found) for $1 \cdot 2\text{H}_2\text{O}$: C 41.34 (41.16), H 3.12 (3.02), N 2.62 (2.86). Crystal structure data for $1 \cdot 4.5\text{MeCN} \cdot 1.5\text{H}_2\text{O}$: $\text{C}_{230}\text{H}_{211.5}\text{Cu}_5\text{Gd}_7\text{N}_{6.5}\text{O}_{83.5}$, $M_w=6596.51$, hexagonal, space group $R\bar{3}$ with $a=b=34.3349(6) \text{ \AA}$, $c=37.9490(7) \text{ \AA}$, $V=38743.8(12) \text{ \AA}^3$, $T=160(2) \text{ K}$, $Z=6$, $R_1 [I > 2\sigma(I)]=0.0506$, $wR_2=0.1236$ (F^2 , all data).
- (8) (a) Langley, S. K.; Moubaraki, B.; Murray, K. S. *Inorg. Chem.* **2012**, *51*, 3947, and references cited therein. (b) Tian, H.; Zhao, L.; Guo, Y.- N.; Guo, Y.; Tang, J.; Liu, Z. *Chem. Commun.* **2012**, 48, 708.
- (9) Mereacre, V.; Ako, A. M.; Clérac, R.; Wernsdorfer, W.; Hewitt, I. J.; Anson, C. E.; Powell, A. K. *Chem. Eur. J.* **2008**, *14*, 3577.
- (10) (a) Baskar, V.; Gopal, K.; Helliwell, M.; Tuna, F.; Wernsdorfer, W.; Winpenney, R. E. P. *Dalton Trans.* **2010**, 39, 4747. (b) Zhang, J.- J.; Hu, S.- M.; Xiang, S.- C.; Sheng, T.; Wu, X.- T.; Li, Y.- M. *Inorg. Chem.* **2006**, *45*, 7173. (c) Leng, J.- D.; Liu, J.- L.; Tong, M.- L. *Chem. Commun.* **2012**, 48, 5286.
- (11) (a) Langley, S.; Chilton, N. F.; Moubaraki, B.; Hooper, T.; Brechin, E. K.; Evangelisti, M.; Murray, K. S. *Chem. Sci.* **2011**, *2*, 1166. (b) Hooper, T. N.; Schnack, J.; Piligkos, S.; Evangelisti, M.; Brechin, E. K. *Angew. Chem. Int. Ed.* **2012**, *51*, 4633.
- (12) (a) Colacio, E.; Ruiz, J.; Lorusso, G.; Brechin, E. K.; Evangelisti, M.; *Chem. Commun.* **2013**, 49, 3845. (b) Wu, M.; Jiang, F.; Kong, X.

The employment of pyridine-2,6-dimethanol in 3d/4f-metal cluster chemistry has resulted in a new $\{\text{Cu}^{\text{II}}_{15}\text{Gd}^{\text{III}}_7\}$ cage-like molecule with a beautiful structure and an overall ferrimagnetic behavior with an appreciable ground state spin value. The compound shows a satisfactory magnetocaloric effect with $-\Delta S_m^{\text{max}} = 22.2 \text{ J kg}^{-1} \text{ K}^{-1}$.

