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'All three-in-one': ferromagnetic interactions, single-molecule magnetism and magnetocaloric properties in a new family of [Cu₄Ln] (Ln^{III} = Gd, Tb, Dy) clusters†

Paul Richardson,^a Dimitris I. Alexandropoulos,^a Luís Cunha-Silva,^c Giulia Lorusso,^d Marco Evangelisti,^d Jinkui Tang^{*b} and Theocharis C. Stamatatos^{*a}

A new family of isomorphous [Cu₄Ln] clusters (Ln^{III} = Gd, Tb, Dy) with a 'propeller'-like topology was obtained from the use of naphthalene-2,3-diol in Cu^{II}/Ln^{III} chemistry; all complexes are ferromagnetically-coupled and display either magnetocaloric properties or SMM behavior depending on the central Ln ion.

The field of inorganic and modern coordination chemistry has been undoubtedly flourished over the last three decades, or so, from the synthesis of new polynuclear metal complexes with aesthetically appealing structures,¹ exciting supramolecular architectures,² and interesting magnetic properties such as ferromagnetism,³ single-molecule magnetism (SMM),⁴ molecular magnetic refrigeration,⁵ and multifunctional materials.⁶ In an ideal case, ferromagnetic interactions result from the accidental orthogonality of the interacting magnetic orbitals of two or more paramagnetic metal ions, especially if these orbitals are the e_g ones.⁷ The magnetic exchange interactions are propagated by the donor atoms (*i.e.*, O atoms) of bridging ligands; it has been established that M–O–M (M = metal) angles close to 90° facilitate the orthogonality of the magnetic orbitals.⁸

Further, when the individual metal ions possess an appreciable number of unpaired electrons, ferromagnetism leads to high-spin molecules. High-spin molecules consisting of isotropic metal ions have shown a remarkable ability to act as magnetic refrigerants.⁹ Magnetic refrigeration is based on the magnetocaloric effect (MCE), *i.e.*, the change of magnetic entropy (ΔS_m) and adiabatic temperature (ΔT_{ad}) following a change of the applied magnetic field (ΔB), and can be used for

cooling purposes *via* adiabatic demagnetization.¹⁰ In contrast, when a high-spin molecule is made of anisotropic metal ions, SMM properties may emerge. SMMs are molecular species that exhibit an energy barrier, *U*, to the relaxation of magnetization.¹¹ Experimentally, an SMM expresses superparamagnet-like properties, showing frequency-dependent out-of-phase alternating-current (ac) magnetic susceptibility signals and hysteresis loops, the diagnostic property of a magnet.

Apparently, a combination of metal ions which fulfills all the above objectives is that of Cu^{II} with primarily Gd^{III} (⁸S_{7/2}, *S* = 7/2, *L* = 0, *g* = 2), and subsequently all paramagnetic and anisotropic Ln^{III} ions (*i.e.*, Tb^{III} and Dy^{III}). In addition, the choice of the organic bridging ligand has been always a challenging task. Such a ligand needs to be able to aggregate the metal ions into a polymetallic motif and simultaneously block the extensive polymerization by providing molecular systems with the necessary thermodynamic stability through, for instance, the chelate effect. To that end, we have decided to employ naphthalene-2,3-diol (ndH₂) chelate¹² in Cu^{II}/4f-metal cluster chemistry as a means of obtaining heterometallic compounds with new structural motifs and interesting magnetic properties. We herein report a new family of isomorphous pentanuclear (NHET₃)₅[Cu₄Ln(nd)₈] (Ln = Gd (**1**), Tb (**2**), Dy (**3**)) clusters resulted from the general reaction of Cu(ClO₄)₂·6H₂O, Ln(ClO₄)₃·xH₂O, ndH₂ and NEt₃ in a 1:1:7:14 ratio in MeOH.† The obtained compounds exhibit a 'propeller'-like topology, they are all ferromagnetically-coupled, and they show either MCE or SMM properties depending on the nature of the Ln^{III} ion. The chemical and structural identities of the complexes were confirmed by single-crystal X-ray crystallography (complete data sets for **1** and **2**), elemental analyses (C, H, N), and IR spectral comparison.†

In view of the structural similarities of **1–3**, only the structure of (NHET₃)₅[Cu₄Gd(nd)₈] (**1**) will be described as a rep-

^aDepartment of Chemistry, Brock University, St. Catharines, Ontario, L2S3A1, Canada. E-mail: tstatamatos@brocku.ca; Tel: (+1)-905-688-5550 Ext. 3400

^bState Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

^cREQUIMTE/LAQV & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal

^dInstituto de Ciencia de Materiales de Aragón (ICMA) and Departamento de Física de la Materia Condensada, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain

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representative example. The molecular structure of the anion of **1** (Fig. 1, top) consists of a central Gd^{III} ion surrounded by four Cu^{II} atoms in a ‘propeller’-like conformation. Eight doubly-deprotonated nd²⁻ ligands serve to bridge the Gd^{III} atom with the outer Cu^{II} atoms using one of the two alkoxido arms; these ligands are thus η¹:η²:μ. The non-bridging O atoms of nd²⁻ are strongly hydrogen-bonded to the Et₃NH⁺ countercations, thus enhancing the overall stability and crystallinity of **1**. Peripheral ligation about the [Cu₄Gd(μ-OR)₈]³⁺ core (Fig. 1, bottom) is provided by the chelating part of the eight naphthalene-2,3-diol groups. The four Cu^{II} atoms occupy the vertices of a distorted, non-planar Cu₄ rectangle (Fig. S1†) while the central Gd^{III} ion is displaced 0.14 Å away from the Cu₄ best-mean-plane. The Cu^{II} atoms are not directly linked to each other but only through the Gd^{III} mediator; hence, there are no significant interactions between the 3d-metal ions. The Cu^{II}–O–Gd^{III} angles span the range 97.1(2)–102.7(2)°.

All Cu^{II} ions are four-coordinate with distorted square planar geometries: the *cis*- and *trans*-angles lie in the 86.3–99.7° and 164.9–174.5° ranges, deviating only slightly from the 90° and 180°, respectively, of an ideal square plane. The tetrahedrality¹³ calculated for Cu1, Cu2, Cu3, and Cu4 in **1** gives average dihedral angles of ~18, ~8, ~11, and ~10°, respectively, supporting the distorted square planar geometry for the basal Cu(1,2,3,4)O₄ planes. The central Gd^{III} is eight-

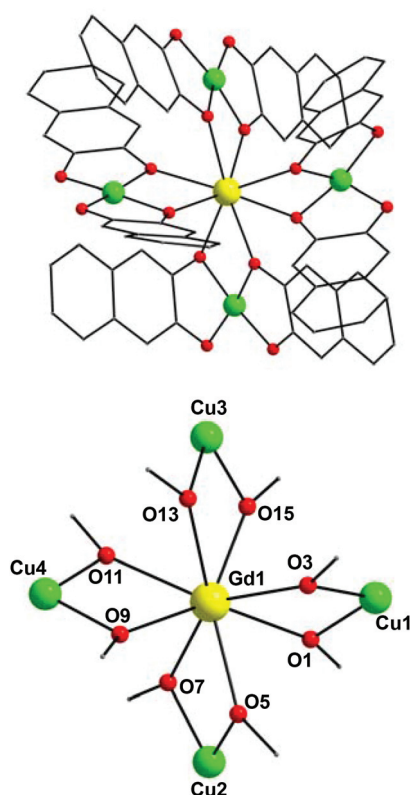


Fig. 1 Molecular structure of the [Cu₄Gd(nd)₈]⁵⁻ anion of complex **1** (top) and its complete, labelled [Cu₄Gd(μ-OR)₈]³⁺ core (bottom). H atoms are omitted for clarity. Color scheme: Cu^{II} green, Gd^{III} yellow, O red, C dark gray.

coordinate with a triangular dodecahedral coordination geometry (CShM value = 0.76, program SHAPE;¹⁴ see Fig. S2 and Table S2†). Tb^{III} ion of complex **2** is also eight-coordinate with triangular dodecahedral coordination geometry (CShM value = 0.81). Finally, the reported compounds join only a handful of previously reported {Cu₄Ln} clusters¹⁵ albeit they are the first ‘propeller’-like clusters exhibiting SMM behaviour and MCE properties (*vide infra*).

Solid-state direct-current (dc) magnetic susceptibility (χ_M) data on dried and analytically-pure samples of **1–3** were collected in the 2.0–300 K range in an applied field of 0.1 T, and are plotted as $\chi_M T$ vs. T in Fig. 2. The experimental $\chi_M T$ values at 300 K for all complexes are in excellent agreement with the theoretical ones expected for four Cu^{II} ($S = 1/2$, $g = 2.2$) and one Gd^{III} (9.69 cm³ K mol⁻¹) or Tb^{III} (13.64 cm³ K mol⁻¹) or Dy^{III} (15.99 cm³ K mol⁻¹) non-interacting ions. The magnetic behaviour of **1–3** indicates ferromagnetic exchange interactions between the Cu^{II} and Ln^{III} centres, with the $\chi_M T$ products steadily increasing with decreasing temperature to reach the values of 17.91 (**1**), 18.72 (**2**), and 21.67 (**3**) cm³ K mol⁻¹ at $T = 2, 3,$ and 2.5 K, respectively. The $\chi_M T$ value of **1** at 2 K is in excellent agreement with the value of 17.88 cm³ K mol⁻¹, expected for an $S = 11/2$ system with $g = 2$. For the anisotropic analogues **2** and **3**, the $\chi_M T$ products slightly decrease below ~3 K, indicating the presence of magnetic anisotropy and/or depopulation of the excited M_J states. For the isotropic analogue **1**, we used the PHI program¹⁶ and the spin-Hamiltonian $H = -J(\hat{S}_{Cu1} \cdot \hat{S}_{Gd1} + \hat{S}_{Cu2} \cdot \hat{S}_{Gd1} + \hat{S}_{Cu3} \cdot \hat{S}_{Gd1} + \hat{S}_{Cu4} \cdot \hat{S}_{Gd1})$ to fit the susceptibility and magnetization data. An excellent fit of the experimental data (solid blue line in Fig. 2) gave as best-fit parameters: $J = +1.31(4)$ cm⁻¹ and $g = 2.00(4)$, thus confirming the intramolecular ferromagnetic interactions between the metal centres and the stabilization of an $S = 11/2$ spin ground state for **1**. Note that the introduction of an additional J -coupling constant, to consider any possible Cu...Cu magnetic interactions, in the above spin Hamiltonian did not improve the fit and gave almost identical $J_{Cu...Gd}$ (+1.36 cm⁻¹) and $J_{Cu...Cu} \sim 0$ cm⁻¹ values. The obtained J value of **1** is of the same order

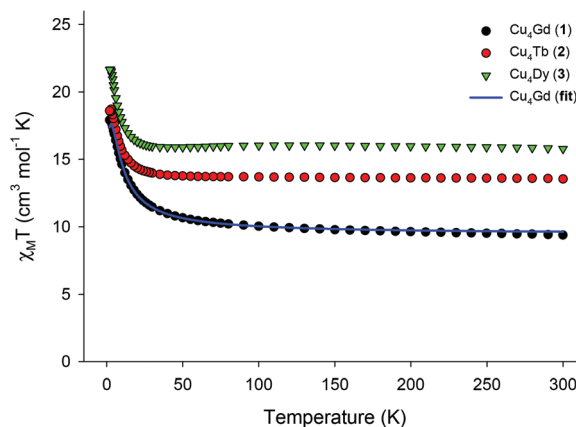


Fig. 2 $\chi_M T$ vs. T plots for **1–3** in an applied field of 0.1 T. Solid blue line is the result of the fit for the Cu₄Gd compound, as described in the text.

of magnitude, although somewhat smaller than those observed in other Cu_4Gd clusters in which the Cu^{II} ions are magnetically coupled to each other ($J_{\text{Cu}\dots\text{Cu}} \neq 0$).¹⁵ The weak ferromagnetic interactions in **1** are likely resulted from the orthogonality of the d and f-metal orbitals.^{8,15,17}

Magnetization (M) vs. field (H) studies for **1–3** (Fig. S3†) show fast saturated variations, further confirming the presence of predominant ferromagnetic interactions in all compounds. The magnetization of **1** at 2 K saturates fast and in small fields to a value of $\sim 11N\mu_{\text{B}}$ consistent with an $S = 11/2$ spin ground state. To evaluate the accuracy of the susceptibility data, the magnetization data of **1** were also fitted using the above spin-Hamiltonian. Best-fit parameters are: $J = +1.34 \text{ cm}^{-1}$ and $g = 2.02$ (Fig. S3†). The M vs. H plots for **2** and **3** between 1.9 and 5 K justify the presence of magnetic anisotropy, since the data are not superimposed on a single master curve.

Given the recent interest in Cu/Gd-metal clusters as low-temperature magnetic coolers,¹⁸ and the large magnetization value of **1** as a result of the ferromagnetic interactions between the metal centres, we decided to pursue magnetocaloric studies. In Fig. 3 we report the magnetic entropy change, $-\Delta S_{\text{m}}$, as derived from heat capacity (Fig. S4,† top) and magnetization data. Values of ΔS_{m} can be obtained from the T and field dependencies of the entropy (Fig. S4,† bottom). The maximum $-\Delta S_{\text{m}}$ for **1** was achieved with $\Delta B = 7 \text{ T}$ at $T = 3 \text{ K}$; however, the obtained value of $\sim 10 \text{ J kg}^{-1} \text{ K}^{-1}$ is much lower than the maximum entropy value per mole ($4.85R \sim 18.43 \text{ J kg}^{-1} \text{ K}^{-1}$) for 4 Cu^{II} and 1 Gd^{III} fully decoupled ions. This indicates that the magnetic coupling between the five metal centres is accountable for the obtained $-\Delta S_{\text{m}}$ value. Indeed, for an $S = 11/2$ spin system the maximum $-\Delta S_{\text{m}}$ expected is given by $R \ln(2S_{\text{T}} + 1) = R \ln 12 = 2.5R \sim 9.5 \text{ J kg}^{-1} \text{ K}^{-1}$; the latter value is in excellent agreement with the experimental $-\Delta S_{\text{m}}$ for **1**, highlighting the effect of the magnitude of J on the MCE.

Ac magnetic susceptibility studies have been also carried out in order to investigate the magnetization dynamics of **2** (Fig. S5†) and **3** in the absence of an external dc magnetic

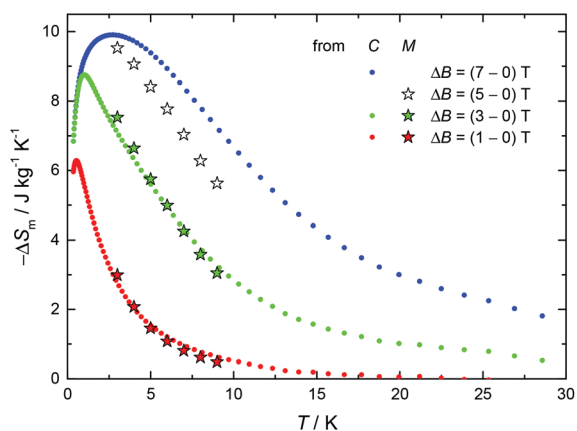


Fig. 3 Magnetic entropy change for Cu_4Gd (**1**), as obtained from heat capacity (C) and magnetization (M) experiments for the indicated applied field changes.

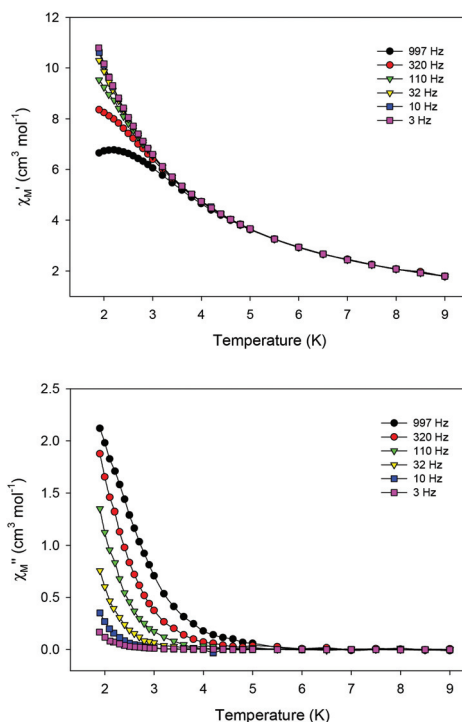


Fig. 4 Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibility signals of **3** in a 3 G field oscillating at the indicated frequencies.

field. Only the Cu_4Dy analogue showed frequency-dependent in-phase (χ'_{M}) and out-of-phase (χ''_{M}) tails of signals at temperatures below $\sim 5 \text{ K}$ (Fig. 4), characteristic of the slow magnetization relaxation of a fast-relaxing SMM with a relatively small energy barrier for the magnetization reversal. Such behavior most likely arises from predominant single-ion effects of the Dy^{III} centre within **3**; note that Dy^{III} is a Kramers ion, and irrespective of the ligand field it is expected to possess a bistable ground state.¹⁹ On the other hand, Tb^{III} is a non-Kramers ion and so its complexes will have a bistable ground state only if it has an axially-symmetric ligand field.¹⁹ Efforts to shift the χ''_{M} tails of signals of **3** to higher temperatures and surpass the fast tunnelling of both **2** and **3** by applying an external dc field are currently in progress.

Conclusions

In conclusion, we have shown that the choice of a capable organic chelating/bridging ligand in Cu/Ln chemistry can provide the means of obtaining new cluster compounds with interesting topologies and diverse magnetic properties, such as high-spin ferromagnetic complexes, SMMs and molecular magnetic refrigerants for low-temperature cooling applications. Work in progress includes the synthesis and complete characterization of the remaining members of this family of Cu_4Ln clusters, the elucidation of their photophysical pro-

perties, and the extension of this research to other polyaromatic diols and 3d/4f-metal combinations.

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