Inorganic Chemistry
Communication
pubs.acs.org/IC

Dodecanuclear $[Cu^{II}_6Gd^{III}_6]$ Nanoclusters as Magnetic Refrigerants

Alina S. Dinca,[†] Alberto Ghirri,[‡] Augustin M. Madalan,[†] Marco Affronte,*,[‡] and Marius Andruh*,[†]

[†]Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie nr. 23, 020464 Bucharest, Romania

[‡]CNR, Institute of nanoSciences S3 and Dipartimento di Fisica, Università di Modena e Reggio Emilia, via G. Campi 213/A, 41100 Modena, Italy

Supporting Information

ABSTRACT: A novel dodecanuclear complex, $[\{(HL)(L)(DMF)Cu^{II}Gd^{III}(DMF)(H_2O)\}_6]\cdot 6DMF$ (**1**; DMF = *N*,*N*-dimethylformamide), has been obtained using the ligand resulting from the condensation of 3-formylsalicylic acid with hydroxylamine (H_3L). The exchange interaction between the phenoxo-bridged Cu^{II} and Gd^{III} ions is weak ferromagnetic ($J = +1.01$ cm^{-1}). The combination of a high-spin ground state with small anisotropy leads to a significant magnetocaloric effect [$-\Delta S_m(0-7\ T) = 23.5$ J K g^{-1} K^{-1} at ~2 K].

The chemistry of heterometallic 3d−4f complexes received a strong impulse from the development of molecular magnetism.[1] The very first $Cu^{II}-Gd^{III}$ compounds illuminating the ferromagnetic interaction between the two metal ions were reported by Gatteschi et al. in 1985[2] and by Okawa et al. in 1990.[3] Both compounds have been obtained using multidentate Schiff-base ligands. Okawa's compound, supposed to be a binuclear complex (Chart S1 in the Supporting Information), has been synthesized by employing a compartmental ligand resulting from a 2:1 condensation between 3-formylsalicylic acid and ethylenediamine. Unfortunately, no crystal structure was reported either for the $[Cu^{II}Gd^{III}]$ complex or for similar complexes with other lanthanides, with the strict binuclear nature of this compound being questionable. The discovery of low-dimensional molecular magnets (single-molecule magnets and single-chain magnets) oriented the interest of chemists and physicists toward the other lanthanides, especially Tb^{III}, Dy^{III}, and Ho^{III}, which have strong magnetic anisotropy, which is a prerequisite for observation of the slow relaxation of the magnetization phenomena.[1,4] More recently, the isotropic Gd^{III} came back to the attention of scientists because of its ability to generate molecular compounds with a large magnetocaloric effect (MCE).[5] MCE implies a temperature drop during the adiabatic demagnetization that can be exploited for refrigeration. Generally speaking, a large MCE is obtained with a highly degenerated magnetic ground state and an easy lift of this degeneration by application of an external magnetic field, which, in turn, induces large entropy variation.[6] One way to obtain this is to get a large spin ground state with small magnetic anisotropy at the same time. In this respect, Gd^{III} is an excellent candidate in the design of molecular magnetic coolers. In addition, a relatively small molecular mass is required to maximize the cooling power available for the external world.[5]

Aiming to get information on the structure of Okawa's compound and, at the same time, to obtain molecules exhibiting a significant MCE, we decided to modify the organic ligand derived from 3-formylsalicylic acid and to react it with Cu^{II} and Gd^{III} ions. The new ligand (H_3L) results from the condensation reaction between 3-formylsalicylic acid and hydroxylamine. Our strategy is based on the observation that two molecules of oxime, one of them with a deprotonated aldoxime group, should generate a supramolecular bicompartmental ligand (Chart S2 in the Supporting Information), which is supported by the well-known hydrogen-bonding interaction observed, for example, in the classical complex of Ni^{II} with dimethylglyoxime. Of course, the assembly of the two organic species (H_2L^- and H_3L) into the supramolecular ligand is favored by the coordination of one or two metal ions. We mention also that the main difference between Okawa's ligand and the supramolecular ligand ($H_2LH\cdots LH_2^-$) resulting from the H_3L and H_2L^- molecules arises from the charges they are carrying after deprotonation: four negative charges in the case of Okawa's ligand and five negative charges for the supramolecular ligand.

The heterometallic complex $[\{(HL)(L)(DMF)Cu^{II}Gd^{III}(DMF)(H_2O)\}_6]\cdot 6DMF$ (**1**; DMF = *N*,*N*-dimethylformamide) was obtained as described in the Supporting Information.

The crystallographic investigation of **1** reveals neutral dodecanuclear clusters, with six Cu^{II} and six Gd^{III} ions (Figure 1a). Details on the crystallographic investigation are given in the Supporting Information. The Cu ion is hosted in the N_2O_2 compartment, showing a square-pyramidal geometry with a DMF molecule occupying the apical position [Cu1−O10 = 2.330(8) Å]. The basal Cu−N and Cu−O distances vary between 1.942(6) and 1.975(10) Å. The Gd ions are coordinated by eight O atoms, showing a square-antiprismatic geometry. The Gd−O distances are in the range 2.347(6)−2.427(7) Å. Each Gd ion is coordinated by two phenoxo and four carboxylato O atoms arising from the oximato ligands, as well as by one water and one DMF molecule. The Gd ion is disposed at 1.379 Å above the plane of the four O atoms from the outer compartment, because of their big size. This makes the main difference between the compartmental ligands derived from 3-formylsalicylic acid and the classical Costes' ligands obtained from *o*-vanillin, in which the methoxy and phenoxo

Received: January 24, 2012
Published: March 12, 2012

dx.doi.org/10.1021/ic3001762 | *Inorg. Chem.* 2012, 51, 3935−3937

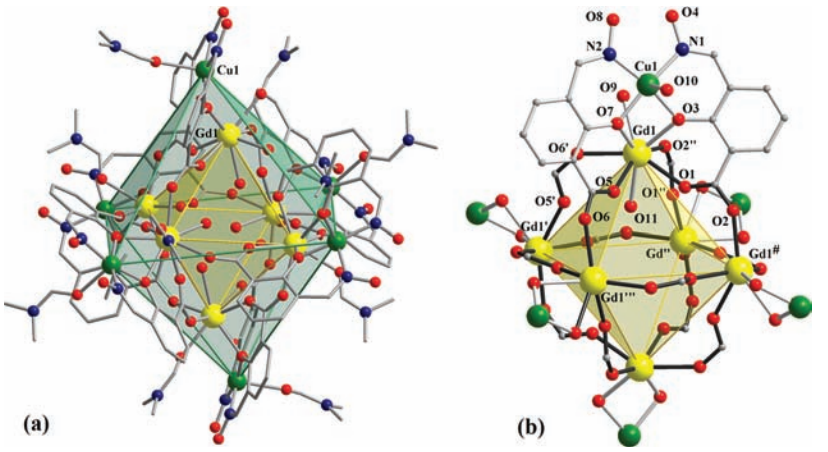

Figure 1. (a) Perspective view of the dodecanuclear cluster **1**. (b) Detail of the molecular structure of **1** showing one supramolecular compartmental ligand and the connectivities between the Gd^{III} ions together with an atom-labeling scheme.

groups delineate a larger compartment able to accommodate the big Ln cations.[7] We recall also that when the second metal is also a 3d metal, with a smaller radius than the Ln, it is coordinated within the plane of the four O atoms.[8] The aggregation of the dodecanuclear cluster occurs through carboxylato bridges: each carboxylato group is coordinated to two Gd ions, with a syn–anti bridging mode (Figures 1b and S1 in the Supporting Information). Each Gd ion is connected by carboxylato bridges to four other Gd ions. The six Gd^{III} ions describe an octahedron that is inscribed into the octahedron generated by the Cu ions. The distance between the phenoxo-bridged Cu^{II} and Gd^{III} ions is 3.3157(13) Å, and the distances between the Gd ions are Gd1···Gd1′ = 5.982 Å, Gd1···Gd1″ = 6.075 Å, Gd1···Gd1‴ = 5.982 Å, and Gd1···Gd1# = 6.075 Å (symmetry codes: ′, $-x + y, -x, z$; ″, $y, -x + y, 2 - z$; ‴, $-y, x - y, z$; #, $x - y, x, 2 - z$).

The magnetic properties of **1** have been investigated. First of all, examination of the $\chi_M T$ vs T curve (Figure 2a) shows the onset of a ferromagnetic interaction between the Cu^{II} and Gd^{III} ions, below 50 K. At room temperature, $\chi_M T(300\ \mathrm{K}) = 49.0$ $\mathrm{cm^3\ mol^{-1}\ K}$ is close to the value expected for six Cu^{II} and six Gd^{III} ions (49.5 $\mathrm{cm^3\ mol^{-1}\ K}$, assuming $g_{Cu} = g_{Gd} = 2$). For $T <$ 2 K, there is no decrease of $\chi_M T$, suggesting that the magnetic interaction between the binuclear {CuGd} moieties within the cluster, if any, is very weak. The magnetization versus field curves have been recorded at different temperatures (Figure S2 in the Supporting Information). At 2 K, the magnetization reaches saturation at 48.3 μ_B, thus suggesting the presence of a $S = 4$ ground state for each {CuGd} moiety. Specific heat C/R versus T curves have been measured in the temperature range 0.3–15 K (Figure 2b). At high temperature, the specific heat is dominated by the lattice contribution, accounted for by the phenomenological law $C_{latt}/R = 234(T/\theta_D)^\alpha$, where $\theta_D = 36$ K and $\alpha = 2.4$.[9] For $T < 10$ K, the magnetic contribution becomes evident; the zero-field curve is generated by two Schottky anomalies, one peaking at about 2 K and another at $T < 0.3$ K, which shows a clear evolution under an applied magnetic field (B).

To quantify the strength of the magnetic interactions, we model the system as six independent {CuGd} pairs, with $S(Cu^{II}) = {}^1/_2$ and $S(Gd^{III}) = {}^7/_2$ ions coupled by the following Hamiltonian (eq 1):

$$H = -JS_{Cu} \cdot S_{Gd} + \mu_B(g_{Cu}S_{Cu,z} + g_{Gd}S_{Gd,z})B \qquad (1)$$

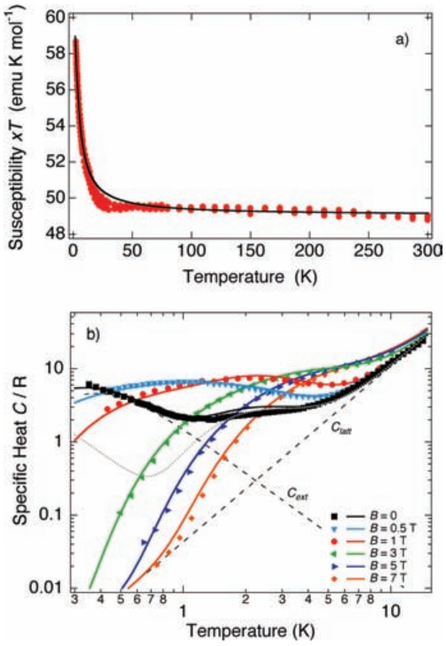

Figure 2. (a) Temperature dependence of the $\chi_M T$ product for **1**. (b) Specific heat versus temperature curves measured under an applied magnetic field for a thin pellet of **1**. The solid lines represent calculations with the parameters reported in the text. The dashed lines in panel b represent distinct contributions to the zero-field specific heat curve due to the lattice (C_{latt}) and extra Schotty anomaly (C_{ext}). The dotted line displays the zero-field specific heat calculated without C_{ext}.

The first term refers to the isotropic exchange interaction between the phenoxo-bridged Cu^{II} and Gd^{III} ions and the second term quantifies the Zeeman interaction with the applied field. The calculated $\chi_M T(T)$ and $[M(B)]_T$ curves, shown respectively in Figures 2a and S2 in the Supporting Information, show good agreement with the set of experimental data by choosing the following parameters: $J = +1.01\ \mathrm{cm^{-1}}$ and $g_{Cu} = g_{Gd} = 2.00$. As a consequence of the ferromagnetic exchange constant, the ground-state multiplet has a spin $S = 4$, while the first excited-state multiplet ($S = 3$) is found at the energy $\Delta E = 4J = 4.04\ \mathrm{cm^{-1}}$.

For simulation of the specific heat curve, we first added an axial anisotropic term $H_{anis} = D_{Gd}[S_{Gd,z}{}^2 - {}^1/_3 S_{Gd}(S_{Gd} + 1)]$, with $D_{\mathrm{Gd}} = -0.02\ \mathrm{cm}^{-1}$,[10] to eq 1. These simulations fit well to the overall experimental $[C(T)]_B$ data, yet it fails to reproduce the bump of the zero-field curve at $T < 1.5$ K (dotted line in Figure 2b) that reveals the effects of weak, but sizable, direct exchange interactions between $\mathrm{Gd^{III}}$ ions. So, to better fit the low-temperature specific heat, we tentatively added an effective two-level Schottky anomaly (C_{ext}) with degeneracy ratio $g_0/g_1 = {}^1/_2$, introducing a phenomenological energy splitting. While more information is required to describe these interactions in details, this numerical fit fixed a maximum limit for $J_{\mathrm{Gd-Gd}}$ of about 0.7 cm^{-1}. Within this simple picture, the magnetic entropy $S_{\mathrm{m}}(T)$ can be calculated from the partition function $Z = \sum_i \mathrm{e}^{-E_i(B)/(k_{\mathrm{B}}T)}$ for fixed B:

$$S_{\mathrm{m}}(T)_B = \left\{ N_{\mathrm{A}} k_{\mathrm{B}} \frac{\partial}{\partial T}(T \ln Z) \right\}_B$$

The entropy change is then $\Delta S_{\mathrm{m}}(T)$ [0−7 T] = $S_{\mathrm{m},0}(T) - S_{\mathrm{m},7\ \mathrm{T}}(T)$. This curve can be compared with ΔS_{m} directly evaluated from the specific heat and magnetization data (Figure 3). Starting from the specific heat, the entropy is calculated according to the formula $S(T)_B = \int (C/T)_B)\ \mathrm{d}T + S_0$, where S_0 is an additive constant that accounts for the experimental "blindness" of the specific heat curve for $T < 0.3$ K and that allows one to match the saturation value at high temperature. The entropy change for compound **1** can also be estimated according to the Maxwell equation, using the magnetization data $\Delta S_{\mathrm{m}}(T)_{\Delta B} = \int [\partial M(T,H)/\partial H]_B\ \mathrm{d}B$.

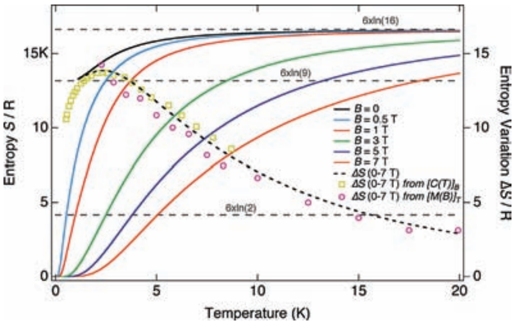

Figure 3. Entropy S/R versus T curves calculated for different magnetic fields B (solid lines). Entropy variation ΔS_{m} for $\Delta H = 0-7$ T (markers). ΔS_{m} [0−7 T] directly evaluated from the specific heat and magnetization experimental data using Maxwell's relations (dashed line).

In Figure 3, the ΔS_{m} values obtained with the different methods compare very well to one another. The entropy saturation is obtained for $T > 10$ K, and it corresponds to the expected value of $6R \ln(16)$. The peak of $\Delta S_{\mathrm{m}}(T)$ is found at about 2.3 K with a maximum value of $\Delta S_{\mathrm{m}}[0-7\ \mathrm{T}] = 13.8R$, in molar units, or $\Delta S_{\mathrm{m}}[0-7\ \mathrm{T}] = 23.5\ \mathrm{J\ kg^{-1}\ K^{-1}}$. This value is comparable to those observed for other $\mathrm{Co^{II}-Gd^{III}}$ complexes recently reported.[5b]

In conclusion, we obtained a novel dodecanuclear $[\mathrm{Cu^{II}}_6\mathrm{Gd^{III}}_6]$ nanocluster showing a significant MCE. This synthetic procedure can be applied for the other lanthanides and can be extended toward luminescent isostructural $[\mathrm{Zn^{II}}_6\mathrm{Ln^{III}}_6]$ clusters. The ability of the new supramolecular bicompartmental oximato ligand to generate various heterometallic complexes is currently under investigation in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, synthesis of compound **1**, crystallographic data, and magnetization versus field curves. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: marius.andruh@dnt.ro (Marius Andruh), marco.affronte@unimore.it (Marco Affronte).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.S.D. acknowledges POSDRU 107/1.5/S/80765 for financial support (a Ph.D. fellowship).

■ REFERENCES

(1) (a) Andruh, M.; Costes, J.-P.; Gao, S. *Inorg. Chem.* **2009**, *48*, 3342. (b) Sessoli, R.; Powell, A. K. *Coord. Chem. Rev.* **2009**, *253*, 2328. (c) Sakamoto, M.; Manseki, K.; Okawa, H. *Coord. Chem. Rev.* **2001**, *219−221*, 379.

(2) Bencini, A.; Benelli, C.; Caneschi, A.; Carlin, R. L.; Dei, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1985**, *107*, 8128.

(3) Matsumoto, N.; Sakamoto, M.; Tamaki, H.; Okawa, H.; Kida, S. *Chem. Lett.* **1990**, 853.

(4) Gatteschi, D.; Sessoli, R.; Villain, J. *Molecular Nanomagnets*; Oxford University Press: Oxford, U.K., 2006.

(5) For example, see: (a) Sessoli, R. *Angew. Chem., Int. Ed.* **2012**, inpress. (b) Evangelisti, M.; Brechin, E. K. *Dalton Trans.* **2010**, *39*, 4672 and references cited therein..

(6) (a) Manoli, M.; Johnstone, R. D. L.; Parsons, S.; Murrie, M.; Affronte, M.; Evangelisti, M.; Brechin, E. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 4456. (b) Evangelisti, M.; Candini, A.; Ghirri, A.; Affronte, M.; Brechin, E. K.; Mcinnes, E. J. L. *Appl. Phys. Lett.* **2005**, *87*, 072504. (c) Zheng, Y.-Z.; Evangelisti, M.; Tuna, F.; Winpenny, R. E. P. *J. Am. Chem. Soc.* **2012**, *134*, 1057. (d) Guo, F.-S.; Leng, J.-D.; Liu, J.-L.; Meng, Z.-H.; Tong, M.-L. *Inorg. Chem.* **2012**, *51*, 405. (e) Evangelisti, M.; Roubeau, O.; Palacios, E.; Camón, A.; Hooper, T. N.; Brechin, E. K.; Alonso, J. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 6606. (f) Zheng, Y.-Z.; Evanghelisti, M.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 3692. (g) Langley, S. K.; Chilton, N. F.; Moubaraki, B.; Hooper, T.; Brechin, E. K.; Evanghelisti, M.; Murray, K. S. *Chem. Sci.* **2011**, *2*, 1166.

(7) Costes, J.-P.; Dahan, F.; Dupuis, A.; Laurent, J.-P. *Inorg. Chem.* **1996**, *35*, 2400.

(8) See, for example, the classical Kahn's heterobimetallics: (a) Kahn, O.; Galy, J.; Journaux, Y.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 2165. (b) Morgenster-Badarau, I.; Rerat, M.; Kahn, O.; Jaud, J. *Inorg. Chem.* **1982**, *21*, 3050.

(9) Evangelisti, M.; Luis, F.; de Jongh, L. J.; Affronte, M. *J. Mater. Chem.* **2006**, *16*, 2534.

(10) Stoian, S. A.; Paraschiv, C.; Kiritsakas, N.; Lloret, F.; Munck, E.; Bominaar, E. L.; Andruh, M. *Inorg. Chem.* **2010**, *49*, 3387.