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Benzoxazole-Based Heterometallic Dodecanuclear Complex $[Dy^{III}_4Cu^{II}_8]$ with Single-Molecule-Magnet Behavior

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Supporting Information

ABSTRACT: Three Cu−Ln (Ln = Dy, Gd, Y) dodecanuclear clusters assembled by a novel ligand of the benzoxazole type are reported. The dysprosium cluster exhibits a frequency dependence of the alternating-current susceptibility and hysteresis loop at low temperature, indicating single-molecule-magnet behavior.

Metal complexes, such as single-molecule magnets (SMMs), exhibiting versatile magnetic behavior have attracted special attention over the past decade.[1,2] The origin of the SMM behavior is the easy-axis (Ising-type) magnetic anisotropy ($D < 0$), which causes the formation of an energy barrier to reorientation of the spin and can be defined in terms of a large-spin ground state and large magnetic anisotropy.[2]

In the search for SMMs, a special position has been attributed to 3d/4f heterometallic complexes where a high-spin ground state and strong magnetic anisotropy may result thanks to a favorable combination of magnetic interactions between the metal centers and the local magnetic anisotropy carried by lanthanide ions such as Dy^{III} and Tb^{III}.[3] A number of such 3d/4f systems have been structurally and magnetically characterized. For example, see Cu/Ln,[4−9] Ni/Ln,[10] Co/Ln,[11] Fe/Ln,[12] Mn/Ln,[13] and Cr/Ln.[14] In this Communication, we report on the synthesis, structure, and magnetic properties of a new series of dodecanuclear molecular wheels, $[Ln^{III}_4Cu^{II}_8]$ [Ln = Dy (**1**), Gd (**2**), Y (**3**)], which were obtained using a ligand of the benzoxazole family.

The reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with ethanolamine, $LnCl_3\cdot 6H_2O$, and $CuCl_2\cdot 2H_2O$ at room temperature and under aerobic conditions in a 2:2:1:2 ratio in the presence of Et_3N leads to the formation of blue-turquoise needlelike crystals with the formula $[Ln_4Cu_8L_8(\mu_2\text{-}H_2O)(\mu_3\text{-}OH)_8Cl_{10}(H_2O)_4]Cl_2\cdot 6MeCN$ [Ln = Dy (**1**), Gd (**2**), Y (**3**); HL = 5,7-di-*tert*-butyl-2-methylenehydroxylbenzoxazole; MeCN = acetonitrile]. The single-crystal X-ray diffraction data collected for all three compounds **1**−**3** show that they are isomorphic.

The crystal structure exemplified hereafter for $[Dy^{III}_4Cu^{II}_8]$ (**1**) consists of a complex cation $[Dy_4Cu_8L_8(\mu_2\text{-}H_2O)(\mu_3\text{-}OH)_8Cl_{10}(H_2O)_4]^{2+}$ crystallizing with two chloride anions for charge balance and molecules of acetonitrile (Figure 1). The cationic entities comprise four Dy^{III} at the vertices of a rhombus and eight Cu^{II} located all around and outside the rhombus. The complete architecture is formed by four slightly distorted heteronuclear $\{Cu_2Dy_2L_2(OH)_2$ cubane-like moieties sharing the Dy^{III} ions in a rhombus fashion. The arrangement of the $\{Dy_2Cu_2L_2(OH)_2\}$ moieties is reminiscent of those reported by us previously for a nonanuclear $[Dy_3Cu_6]$ but sharing the Dy^{III} in a triangular fashion.[4] A lateral look at the cluster shows four Dy^{III} ions sandwiched between two squares, each made of four Cu^{II} centers, with Cu···Cu distances of 5.164, 6.505 Å and 5.623, 6.930 Å and Cu−Cu−Cu angles of 89.40−90.60° (Figures 1 and S2 in the Supporting Information).

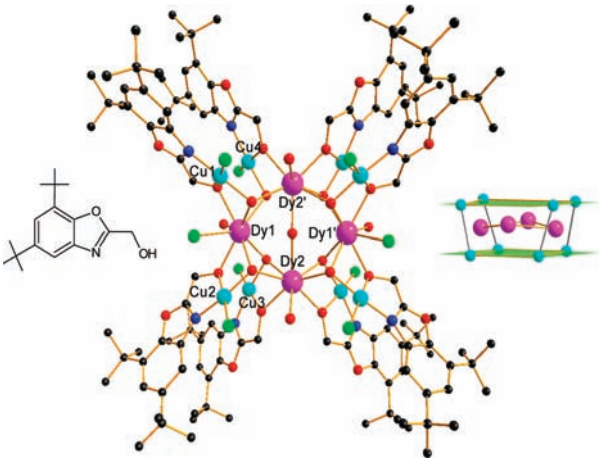

Figure 1. Structure of the cation $[Dy_4Cu_8L_8(\mu_2\text{-}H_2O)(\mu_3\text{-}OH)_8Cl_{10}(H_2O)_4]^{2+}$ with scheme of the ligand and view of the Dy^{III} ions sandwiched between the Cu^{II} ions. The solvent molecules and hydrogen atoms are omitted for clarity.

Eight oxygens from the alkoxo groups of the deprotonated ligand L^- and eight oxygen atoms from the hydroxo groups bridge the Dy^{III} and Cu^{II} metal ions in a μ_3 fashion. Each alkoxo group connects one Cu^{II} center with one Dy^{III} ion, and each hydroxo group links two Dy^{III} ions to one Cu^{II} ion. One molecule of water is found in the center of the cluster located on a C_2 axis and bridging two symmetrically related Dy^{III} ions in a μ_2 fashion.

Each of the four Dy^{III} ions are eight-coordinate. Seven positions come from four bridging hydroxo groups, two alkoxo groups of the deprotonated ligand L^-, and one coordinated water molecule. The eighth position is occupied differently by a chloride ion for the Dy1 ions, while it is a bridging water molecule

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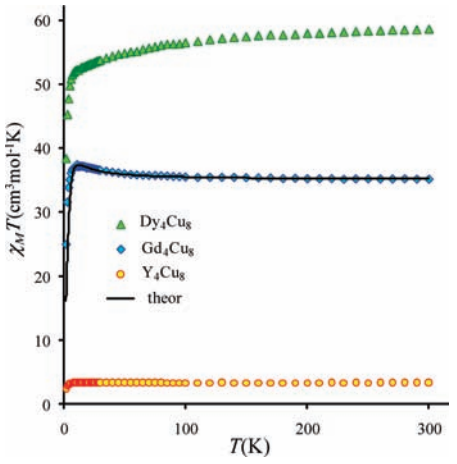

Figure 2. $\chi_M T$ vs T plot data for **1**−**3**. The black solid lines correspond to the simulation according the Hamiltonian with parameters described in the text.

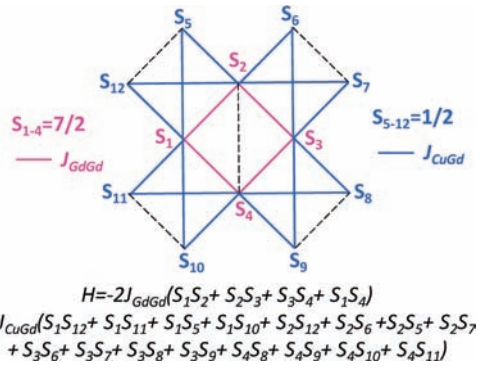

Figure 3. Spin topology and Hamiltonian for cluster **2** (Gd_4Cu_8).

for the Dy2 ions (Figure S4 in the Supporting Information). Each of the Cu^{II} ions is coordinated in the plane by one nitrogen and one oxygen atom of a benzoxazole ligand {CuL} plus one hydroxo group and one chloride ion. The Cu−O, Cu−N, and Cu−Cl bond lengths are 1.921−2.020, 1.962−1.993, and 2.252−2.260 Å, respectively. An oxygen atom from a bridging alkoxo group belonging to the adjacent {CuL} unit is also found in the apical position. However, it is rather far at distances ranging from 2.304 to 2.923 Å. There are also two molecules of acetonitrile at 2.702 Å on the sixth position of Cu4 and Cu4′. These distances are also rather long. Thus, all Cu^{II} ions are viewed to have the same environment, which is best described as square-planar.

The temperature dependences of the magnetic susceptibility for **1**−**3** were measured on polycrystalline samples in the temperature range 2−300 K under an applied magnetic field of 0.1 T and are shown in Figure 2. The value of $\chi_M T$ (3.30 $cm^3 \cdot K \cdot mol^{-1}$) for **3** at room temperature is in good agreement with the calculated value of 3.308 $cm^3 \cdot K \cdot mol^{-1}$ for eight Cu^{II} ions ($S = {}^1/_2$ with $g = 2.10$). The variation of $\chi_M T$ with temperature is constant, as was expected for noninteracting Cu^{II} ions, in agreement with the presence of square-planar Cu^{II} in isolated {CuL} units. The decrease of $\chi_M T$ at low temperature (3 K) is most probably due to the effect of intermolecular interactions and/or weak Cu−Cu interactions.

The magnetization curves for **3** can be well fitted with a Brillouin function for eight Cu^{II} ions ($S = {}^1/_2$ with $g = 2.10$) and is consistent with negligible values for the Cu−Cu interaction (Figure S5 in the Supporting Information).

The $\chi_M T$ value for **2** at room temperature is 35.15 $cm^3 \cdot K \cdot mol^{-1}$ (Figure S6 in the Supporting Information) and agrees well with the expected value of 35.13 $cm^3 \cdot K \cdot mol^{-1}$ for four Gd^{III} ions ($^8S_{7/2} = {}^7/_2$ with $g = 2$) and eight Cu^{II} ions ($S = {}^1/_2$ with $g = 2.10$) in accordance with the Cu^{II} values extracted from the corresponding yttrium analogue. Upon cooling, the $\chi_M T$ product increases to a maximum value of 37.11 $cm^3 \cdot K \cdot mol^{-1}$ at 10 K and 0.1 T. Below 10 K, the $\chi_M T$ product sharply decreases and reaches the value of 25.04 $cm^3 \cdot K \cdot mol^{-1}$ at 2 K. This behavior indicates the presence of both ferromagnetic and antiferromagnetic interactions. According to the X-ray diffraction investigation on single crystals, clusters **1**−**3** are isomorphous. Thus, as for compound **2**, we can also neglect the Cu−Cu interaction and use the following isotropic spin Hamiltonian for simulation of the magnetic susceptibility for (Figure 3):[15] where J_{GdGd} and the first term of the Hamiltonian address the magnetic interaction in the central Gd_4 core (rhomb) and J_{CuGd} and the second term hold for the magnetic interaction between Cu and Gd. Because of the similarity of the bridging functions for all Cu/Gd pairs and to avoid overparameterization, we used only one common parameter (J_{GdGd} and J_{CuGd}) for each of the Gd−Gd and Cu−Gd magnetic interactions (Figure 3). The estimated J values can be found by simulation of the $\chi_M T$ and magnetization curves using the indicated Hamiltonian.[15] The best coincidence of the experimental and calculated values of the χT product and magnetization is obtained for $J_{GdGd} = -0.15\ cm^{-1}$, $J_{GdGd} = +0.5\ cm^{-1}$, $zJ = -0.019\ cm^{-1}$, and $g = 2.10$ (see Figures 2 and S6 in the Supporting Information), which correspond, as may be expected, to a weak antiferromagnetic Gd−Gd magnetic interaction and a weak ferromagnetic Cu−Gd interaction.[16]

The product of $\chi_M T$ for compound **1** at $H = 0.1$ T decreases from 58.55 $cm^3 \cdot K \cdot mol^{-1}$ at room temperature to 38.14 $cm^3 \cdot K \cdot mol^{-1}$ at 2.0 K (Figure 2). The value at room temperature is close to the expected value of 59.99 $cm^3 \cdot K \cdot mol^{-1}$ for four Dy^{III} ions ($^6H_{15/2}$, $L = 5$, and $g = {}^4/_3$)[17] and eight Cu^{II} ions ($S = {}^1/_2$ with $g = 2.10$). The experimental values for the field dependence of magnetization at 2 and 5 K for **1** are typical and indicate the presence of anisotropy in compound **1** (Figure S7 in the Supporting Information). Alternating-current (ac) magnetic susceptibility measurements performed in a 2−12 K range using a 2.7 G ac field oscillation in a 1−1400 Hz frequency range for compound **1** are depicted in Figure S8 in the Supporting Information. The temperature dependence of the in-phase susceptibility shows frequency dependence but without maxima as a result of either a low-energy barrier of magnetic relaxation or tunneling. The application of a small direct-current (dc) field in the range 0.01−0.1 T does not change the ac signal profile, suggesting that the slow magnetic relaxation (at 2 K) is not influenced by tunneling effects. The presence of a slow magnetic relaxation for **1** suggests the SMM behavior.

To confirm the SMM behavior, the magnetization versus applied dc field data were collected on single crystals of **1** using a micro-SQUID apparatus at the 0.04−0.6 K range.[18] This revealed hysteresis loops, whose coercivity was temperature- and sweep-rate-dependent, increasing upon cooling and with an increase in the field sweep rate, respectively, as was expected for the superparamagnetic-like behavior of an SMM (Figure 4 and Figure S9).

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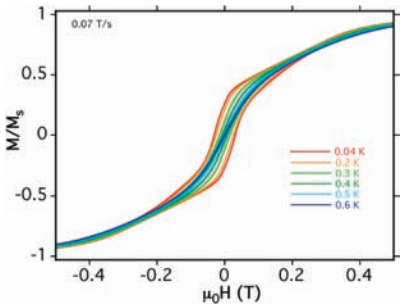

Figure 4. Plot of normalized magnetization (M/M_s) vs applied field ($\mu_0 H$) for **1** (Dy_4Cu_8). The loops are shown at different temperatures at 0.07 $T \cdot s^{-1}$.

The Dy_4 core in **1** is clearly responsible for this SMM behavior. The shape of the hysteresis loops and the cluster topology core is quite similar to that previously reported for a $[Dy_4Cr_4]$ system,[14] suggesting that there is an analogous orientation of the main anisotropy axes in the central Dy_4 core.

In conclusion, a new series of dodecanuclear heterometallic Cu^{II}/Ln^{III} [Ln = Dy (**1**), Gd (**2**),Y (**3**)] clusters using benzoxazole-type ligands are reported. For **2**, magnetic data reveal the presence of ferromagnetic Cu−Gd and antiferromagnetic Gd−Gd interactions. The frequency dependence of the ac signals and magnetization hysteresis loop suggests that complex **1** is a new SMM.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedure and crystallographic refinement details for **1**−**3**, the packing of clusters in the crystal lattice, and additional magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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