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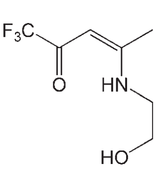
A Nonanuclear Dysprosium(III)–Copper(II) Complex Exhibiting Single-Molecule Magnet Behavior with Very Slow Zero-Field Relaxation**

Christophe Aronica, Guillaume Pilet,
Guillaume Chastanet, Wolfgang Wernsdorfer,
*Jean-François Jacquot, and Dominique Luneau**

The discovery that some metal coordination clusters may behave as single-molecule magnets (SMMs)[1–4] is currently stimulating abundant research in relation to potential applications in information processing and storage.[5] Indeed, SMMs are molecules that can be magnetized in a magnetic field and retain the magnetization when it is switched off. As a consequence, they may show hysteresis loops reminiscent of magnets.[2] In metal clusters, such behavior results from a strong magnetic ground state with large negative axial anisotropy ($D<0$)[6,7] and induces two possible orientations (up and down), between which the magnetization can fluctuate. The fluctuation rate, also named relaxation, depends on the energy barrier U that separates the orientations. In the case of an ideal ground spin state S well separated from the excited states, U is equal to $-DS^2$ for an integer spin and $-D(S^2-{}^1\!/_4)$ for a half-integer spin ($D<0$). Therefore, the larger the D and S values are, the higher the barrier is and the longer the magnetization is retained. This barrier can be thermally overcome or shortcut by quantum tunneling of magnetization (QTM).[8] This tunneling trough the barrier contributes to accelerating the overall relaxation process. In practice, coexistence of the two processes leads to an experimental effective barrier U_{eff} defined by an Arrhenius law: $\tau=\tau_0\exp(U_{\text{eff}}/kT)$.[9] One of the main goals of current research is to achieve long relaxation times τ, which are crucial for information storage applications.[10,11]

In this context, the use of lanthanide ions, such as Dy^{III} and Tb^{III}, has many advantages. Indeed, their large spins and pronounced spin–orbit coupling result in strong Ising-type magnetic anisotropy.[12] Recent reports have shown that even some of their mononuclear complexes may behave as SMMs.[13,14] During this work, a Dy^{III}_3 trinuclear cluster was also reported to exhibit slow relaxation despite its near diamagnetic ground state.[15] Moreover, the combination of 3d and 4f transition-metal ions may increase the ground spin state through d–f magnetic interactions.[16–20] Lanthanides have high coordination numbers and geometries, which may be useful for engineering large polynuclear clusters, and their potential optical properties are of interest to prospective multifunctional materials.[21,22]

With this in mind, and as part of our work on polynuclear metal complexes,[23,24] we chose the Schiff base 1,1,1-trifluoro-7-hydroxy-4-methyl-5-azahept-3-en-2-one (LH_2, Scheme 1). Such Schiff bases are known to give cubane-like clusters with Cu^{II} ions.[25,26] By using a mixture of copper(II) and lanthanide(III) ions, we succeeded in synthesizing a family of heterobimetallic nonanuclear clusters $[\text{Ln}^{\text{III}}_3\text{Cu}^{\text{II}}_6]$ for most lanthanide ions. Herein, we report the synthesis, crystal structure, and magnetic properties of the nonanuclear $\text{Dy}^{\text{III}}\text{Cu}^{\text{II}}$ compound $[\text{Dy}^{\text{III}}_3\text{Cu}^{\text{II}}_6\text{L}_6(\mu_3\text{-OH})_6(\text{H}_2\text{O})_{10}]\text{Cl}_2\cdot\text{ClO}_4\cdot 3.5\,\text{H}_2\text{O}$ ($[\text{Dy}_3\text{Cu}_6]$), which exhibits SMM behavior.



Scheme 1. Schiff base LH_2.

The crystal structure of $[\text{Dy}_3\text{Cu}_6]$ consists of cationic entities $[\text{Dy}^{\text{III}}_3\text{Cu}^{\text{II}}_6\text{L}_6(\mu_3\text{-OH})_6(\mu_1\text{-H}_2\text{O})_{10}]^{3+}$ (Figure 1 a), uncoordinated chloride and perchlorate anions for charge balance, and water molecules of crystallization. The cationic cluster $[\text{Dy}^{\text{III}}_3\text{Cu}^{\text{II}}_6\text{L}_6(\mu_3\text{-OH})_6(\text{H}_2\text{O})_{10}]^{3+}$ (Figure 1 a) is built from three Dy^{III} ions arranged in a triangular fashion with $\{\text{Cu}^{\text{II}}_2\text{L}^{2-}_2\}$ dimer units on each edge of the triangle (Figure 1 b,c). Six alkoxo oxygen atoms of the deprotonated ligands L^{2-} and six OH groups bridge the different metal ions in a μ_3 fashion (Figure 1 c). The six OH groups connect the Dy^{III} ions within the triangular framework $\{\text{Dy}^{\text{III}}_3(\text{OH})_6\}$ and with the Cu^{II} ions of adjacent $\{\text{Cu}^{\text{II}}_2\text{L}^{2-}_2\}$ dimer units. One alkoxo bridge connects the Cu^{II} ions within the $\{\text{Cu}^{\text{II}}_2\text{L}^{2-}_2\}$ dimer units and the second bridge with adjacent Dy^{III} ions (Figure 1 b). This behavior affords distorted $\{\text{Cu}_2\text{L}_2\text{Dy}_2(\text{OH})_2\}$ cubane-like moieties in a similar way to homometallic cubane-like compounds.[25,26] The cationic entity can also be described as resulting from condensation of three distorted $\{\text{Dy}_2\text{Cu}_2\text{O}_4\}$ cubane-like moieties that share the Dy^{III} ions in a triangular fashion. The structural features of the $\{\text{Cu}_2\text{L}_2\text{Dy}_2(\text{OH})_2\}$ moieties (Figure 1 c) are reminiscent of those reported for a $[\text{Dy}_2\text{Cu}_2]$ complex, but in our case the Cu^{II} moieties form dimers.[27] The $\{\text{Dy}_2\text{Cu}_2\text{O}_4\}$ cubane-like moieties have small (av.: 3.4 Å) and large (av.: 3.7 Å) Dy⋯Cu distances. The cationic entities are well isolated from each other, as no relevant hydrogen bonds were found between them.

The three Dy^{III} ions have the same eight-coordinate environment formed by the oxygen atoms of two coordinated water molecules, four bridging OH groups, and two bridging alkoxo groups of the ligand L^{2-}. The $\text{Dy}^{\text{III}}\text{–O}$ bond lengths

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[*] C. Aronica, Dr. G. Pilet, Dr. G. Chastanet, Prof. D. Luneau
Université Claude Bernard Lyon-1
Laboratoire des Multimatériaux et Interfaces (UMR 5615)
Campus de La Doua, 69622 Villeurbanne Cedex (France)
Fax: (+33) 472-431-160
E-mail: luneau@univ-lyon1.fr
Dr. W. Wernsdorfer
Laboratoire Louis Néel, CNRS-BP 166
25 Avenue des Martyrs, 38042 Grenoble, Cedex 9 (France)
J.-F. Jacquot
CEA-Grenoble, DRFMC, Service de Chimie Inorganique et Biologique
17 rue des Martyrs, 38054 Grenoble, Cedex 9 (France)

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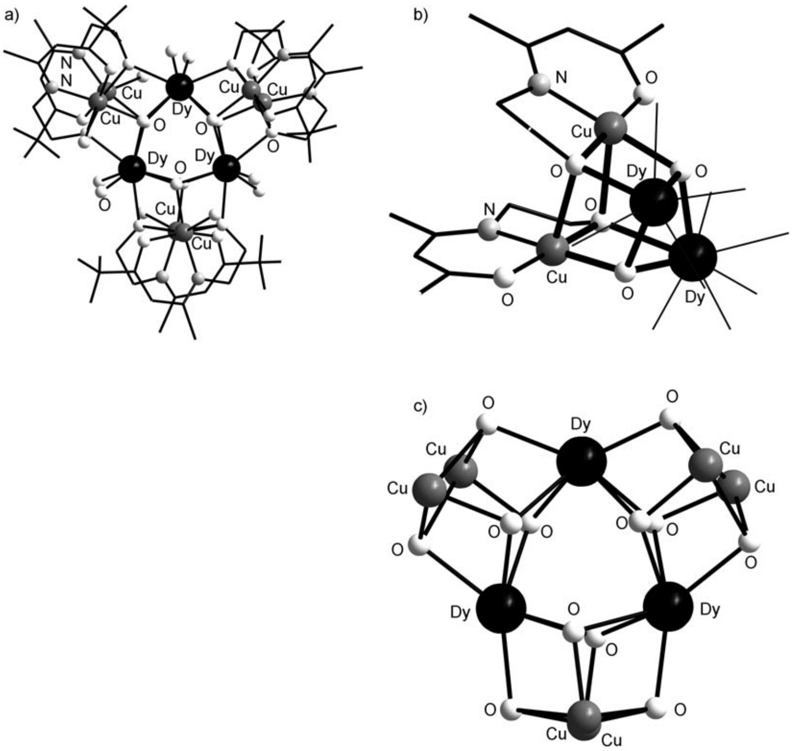

Figure 1. Structure of the cation $[Dy^{III}_3Cu^{II}_6L_6(\mu_3\text{-}OH)_6(H_2O)_{10}]^{3+}$ (a) with fragments showing the $\{Cu_2L_2Dy_2(OH)_2\}$ cubane-like moieties (b) and the alkoxo/hydroxo-bridged metal framework $\{Cu_6Dy_3O_{12}\}$ (c). Selected distances [Å]: Dy···Dy 3.7885(6), 3.8165(5), 3.8201(6); Dy···Cu 3.390(1), 3.401(1), 3.624(1), 3.685(1), 3.399(1), 3.410(1), 3.676(1), 3.703(1), 3.389(1), 3.401(1), 3.632(1), 3.646(1); Cu···Cu 3.195(2), 3.138(2), 3.150(2).

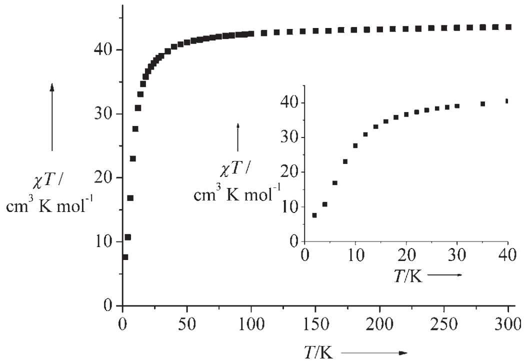

Figure 2. Temperature dependence of χT for $[Dy_3Cu_6]$. The inset shows the low-temperature behavior.

(2.287(6)–2.45(6) Å, av.: 2.38 Å) are normal and in good agreement with calculated values.[28] Within the triangular framework $\{Dy^{III}_3(OH)_6\}$ the $Dy^{III}\cdots Dy^{III}$ distances are in the range 3.7885(6)–3.8201(6) Å.

The six Cu^{II} ions all have the same basic five-coordinate environment. The basal plane is made up of two oxygen atoms and one nitrogen atom from the ligand L^{2-} plus one oxygen atom of an hydroxo group with Cu–O and Cu–N bond lengths of 1.905(7)–1.989(6) and 1.942(8)–1.954(8) Å, respectively. The axial position is occupied by an oxygen atom from the bridging alkoxo group belonging to the second $\{Cu^{II}L^{2-}\}$ moiety of the $\{Cu^{II}_2L^{2-}_2\}$ dimer. As is generally found in cubane-like compounds,[25,26,29] this axial Cu–O(alkoxo) bond is long (2.505(8)–2.748(7) Å) and the Cu-O(alkoxo)-Cu bond angles are close to orthogonality (82.6–90.5(3)°). Moreover, among the six Cu^{II} ions, four have an additional coordinated water molecule in the sixth position with a long bond (2.84(2)–2.579(8) Å) to form an elongated octahedron. No such sixth ligand was found for two of the Cu^{II} ions, and coordination of perchlorate or chloride anions to the two other Cu^{II} ions is excluded, as the smallest $Cu\cdots O_4Cl$ and Cu···Cl distances are 5.490 and 5.233 Å, respectively. Within the three $\{Cu_2^{II}L^{2-}_2\}$ dimer units (Figure 1b), the Cu···Cu distances are in the range 3.138(2)–3.195(2) Å.

The temperature dependence of the magnetic susceptibility was measured on a polycrystalline sample in the temperature range 2-300 K at 1 kOe (Figure 2). At 300 K, the χT value of 43.56 cm^3 K mol^{-1} is close to that of 44.75 cm^3 K mol^{-1} expected for six Cu^{II} (2.25 cm^3 K mol^{-1}) plus three Dy^{III} ions (42.5 cm^3 K mol^{-1}) in a $H_{15/2}$ ground state ($J = 15/2$, $g = 4/3$). On cooling, χT decreases slowly down to 50 K and then drops sharply to reach 7.57 cm^3 K mol^{-1} at 2 K, at which it shows an inflection. This behavior is ascribed to the effect of the exchange interactions between the metal ions (Cu···Cu, Cu···Dy, and Dy···Dy) combined with the crystal-field effect, which is important for Dy^{III}. At present, it is not possible to quantify the different contributions, but the field effect is expected to be dominant. The Cu···Cu exchange should be zero or weakly ferromagnetic. Indeed, considering the structural features (see above) the Cu-O(alkoxo)-Cu bridges within the $\{Cu_2^{II}L_2\}$ dimer units should not favor strong overlap[30] and, in agreement with homometallic Cu^{II} cubane-like compounds, this should give weak ferromagnetic coupling.[25,26,29] The Dy···Dy and Dy···Cu interactions are expected to be small, as is generally the case for exchange coupling with lanthanides and as has been argued for the related $[Dy_2Cu_2]$,[27] in which the structural features are comparable with those found for $[Dy_3Cu_6]$ (av.: Dy···Dy 3.94, av.: Cu···Dy 3.32 and 3.70 Å). Previously, it was found that weak antiferromagnetic interactions between lanthanide(III) ions arranged in a triangular configuration may lead to a diamagnetic ground state.[15,31] This is not the case in $[Dy_3Cu_6]$, and we believe that the Cu···Cu and moreover the Cu···Dy couplings while small are responsible for the non-vanishing susceptibility at low temperature and the peculiar magnetic behavior.

At 2 K, the field dependence of the magnetization of polycrystalline samples exhibits an unusual two-step feature (Figure 3a). The first step, which reaches an approximate magnetization of 6–7 μ_B at 10 kOe, is followed by a second step that slowly increases to 19 μ_B at 50 kOe. This value is consistent with that expected for six Cu^{II} and three Dy^{III} ions with an effective spin of $S = \frac{1}{2}$ and a g value between 8 and 10 at low temperature. The intermediate saturation value of about 6 μ_B, which corresponds to a fraction of the overall value (19 μ_B), is reminiscent of "canting" in bulk magnets. It is ascribed to the interplay of the different exchange couplings (Cu···Cu, Dy···Cu, and Dy···Dy) being overcome at higher

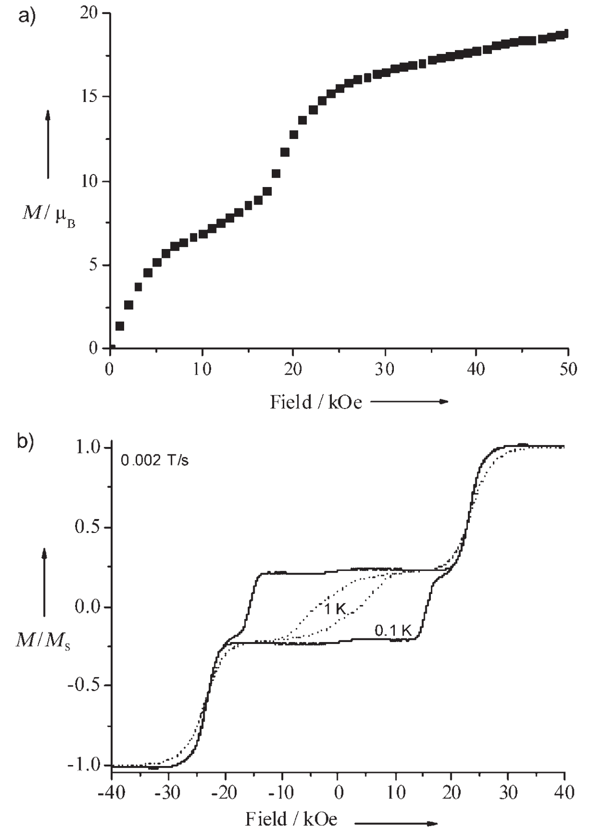

Figure 3. Magnetization curves for [Dy_3Cu_6]. a) Polycrystalline sample at 2 K; b) single crystal (μ-SQUID) at 1 K (dashed) and 0.1 K (solid line). Scan rate: 0.002 Ts^{-1}.

field. This value (6 μ_B) is in agreement with the χT value at low temperature (ca. 7 $cm^3 K mol^{-1}$) for a ground state with $S \approx 3$.

Single crystals of [Dy_3Cu_6] were further studied by the Micro-SQUID technique[7] in the temperature range 1.1–0.04 K. A stepped shape of the magnetization curve is also observed (Figure 3b), in agreement with measurements on polycrystalline samples. Below 1.1 K, hysteresis loops are observed, but only for the first step, with large coercive field widening on cooling ($H_c = 15$ kOe at 0.1 K). This behavior is typical of an SMM with very slow zero-field relaxation. The absolute value of the magnetization, which is not accessible with this technique, was estimated from the measurement at 2 K on the polycrystalline sample (see above). At this temperature, complete saturation was not reached, but we can estimate the magnetization of the first step to be close to 6–7 μ_B. Again the presence of this step exhibiting hysteresis loops at low temperature is quite unusual. It is in contrast with [Dy^{III}_3].[15] Despite the difficulty in quantifying the contributions of the different interactions, this behavior may be ascribed to the anisotropy of the Dy···Cu magnetic exchange, which could force the resulting anisotropy to be out of the plane. It is in agreement with previous studies on [$DyCu_4$] and [Dy_2Cu] complexes showing that Dy^{III}–Cu^{II} exchange coupling causes strong anisotropy.[19,32] This anisotropy can lead to strong "canting", responsible for the nonvanishing magnetic moment in contrast to [Dy^{III}_3].[15]

Studying the magnetization relaxation by ac susceptibility revealed a strong frequency dependence of χ' and χ'' below 5 K, as expected for an SMM (Figure 4). The relaxation time τ was extracted from the maximum of χ'' at different frequencies ($\tau = 1/\omega$) between 1.8 and 4 K and by decay measurements of the dc magnetization at different temperatures in the range 1.8–0.04 K.[33] (See the Supporting Information for a plot of τ values versus $1/T$.) A linear fit performed in the high-temperature regime to the Arrhenius equation $\tau = \tau_0 \exp(U_{eff}/k_B T)$ gave the dynamical parameters $U_{eff} = 25$ K and $\tau_0 = 1.5 \times 10^{-7}$ s.

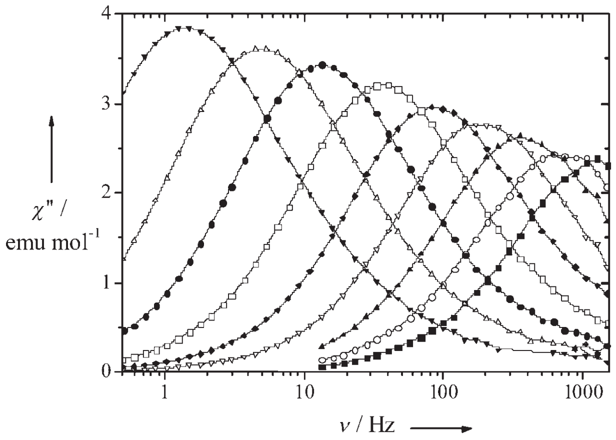

Figure 4. Frequency dependence of the out-of-phase magnetic susceptibility χ'' at different temperatures.

In summary, the dysprosium–copper nonanuclear complex reported herein exhibits features typical of SMMs, that is, both hysteretic behavior of the magnetization and frequency dependence of the ac magnetic susceptibility. From prior studies the ground spin state of [Dy_3Cu_6] is expected to be $S = 3$ with an anisotropy barrier of 25 K associated with a slow zero-field relaxation and a large coercive field. Further experiments are underway to quantify the different contributions to this behavior, such as studies on analogues with diamagnetic lanthanide ions, by EPR spectroscopy, with polarized neutrons, and theoretical calculations. Such understanding is required to improve the synthetic strategy. Nevertheless, [Dy_3Cu_6] is at present one of the best single-molecule magnets and demonstrates the ability of the 3d–4f heterometallic strategy to increase S and D and consequently the relaxation time.

Experimental Section

Synthesis: All chemicals and solvents were used as received; all preparations and manipulations were performed under aerobic conditions. The Schiff base ligand LH_2 was obtained by condensation of ethanolamine with 1,1,1-trifluoro-2,4-pentanedione in methanol by a previously reported method.[34,35]

[Dy_3Cu_6] was obtained in a one-pot reaction by mixing LH_2, [$Dy(ClO_4)_3$], and $CuCl_2$ in methanol in the presence of triethylamine. LH_2 (0.2 g, 1.02 mmol) was dissolved in methanol (10 mL) and [$Dy(ClO_4)_3$]·6H_2O (0.26 g, 0.56 mmol) in methanol (10 mL) was added dropwise with stirring over 10 min. A solution of $CuCl_2$·2H_2O

(85 mg, 0.50 mmol) in methanol (5 mL) was added to the resulting clear yellow solution. The solution turned clear green and stirring was maintained for 5 min. Finally, triethylamine (0.2 mL) was added to the reaction mixture to give a deep-blue solution. One week of slow evaporation gave 125 mg of square-plate blue single crystals suitable for X-ray diffraction, which were isolated by filtration and washed with a small amount of methanol (60 % yield based on Cu). Elemental analysis (%) calcd for $C_{42}H_{81}Cl_3Cu_6Dy_3F_{18}N_6O_{35.50}$: C 19.74, H 3.20, Cl 4.16, Cu 14.92, Dy 19.08, F 13.38, N 3.29; found: C 19.86, H 2.94, Cl 3.72, Cu 14.23, Dy 18.34, F 12.31, N 3.21.

Caution: Although we have not experienced any problems in this work, perchlorate salts may be explosive and should be handled with great care.

Crystal data for $[Dy_3Cu_6]$: $C_{42}H_{81}Cl_3Cu_6Dy_3F_{18}N_6O_{35.50}$, $M = 2555.2\,\mathrm{g\,mol^{-1}}$, space group $P2_1/c$ (No. 14), $a = 17.7136(4)$, $b = 20.6244(4)$, $c = 24.5220(5)$ Å, $\beta = 108.352(1)°$, $V = 8503.0(3)$ Å^3, $Z = 4$, $\rho = 1.996\,\mathrm{g\,cm^{-3}}$, $\mu = 4.283\,\mathrm{mm^{-1}}$, $F(000) = 4976$. 33465 measured reflections[36] collected ($R_{int} = 0.033$) at 150 K on a Nonius KappaCCD diffractometer with monochromatic $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). 1027 refined parameters for 10701 unique reflections. Solution with SIR97;[37] refinements with CRYSTALS.[38] Final R indices ($I > 3\sigma(I)$): $R(F) = 0.0518$, $Rw(F^2) = 0.0619$. CCDC 297249 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic measurements: dc measurements were performed on polycrystalline samples with a Quantum Design SQUID magnetometer. To avoid orientation in the magnetic field, the dysprosium samples were pressed in a teflon sample holder equipped with a piston. The magnetic susceptibility was measured in the temperature range 2–300 K in a field of 1 kOe. The magnetization was measured at 2 K in the range 0–5.5 kOe.

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