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Article (Accepted Version)

Kühne, Irina A, Kostakis, George, Anson, Christopher E and Powell, Annie K (2016) An undecanuclear ferrimagnetic Cu<sub>9</sub>Dy<sub>2</sub> SMM achieved through ligand fine-tuning. *Inorganic Chemistry*, 55 (9). pp. 4072-4074. ISSN 0020-1669

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# An undecanuclear ferrimagnetic Cu<sub>9</sub>Dy<sub>2</sub> SMM achieved through ligand and fine-tuning

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**KEYWORDS** single molecule magnet, topology, copper, lanthanide, coordination cluster.

## Supporting Information Placeholder

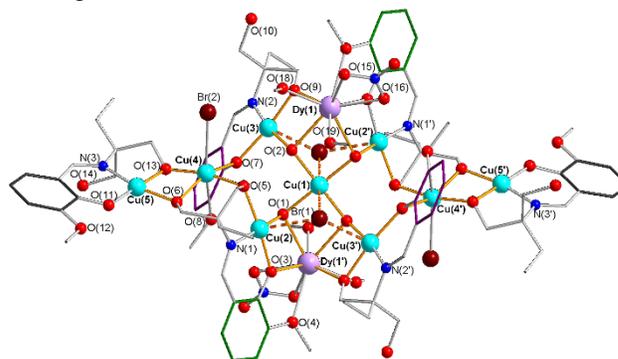
**ABSTRACT:** We describe the concept of increasing the nuclearity of a previously reported high-spin Cu<sub>5</sub>Gd<sub>2</sub> core using a “fine tuning” ligand approach. Thus two Cu<sub>9</sub>Ln<sub>2</sub> coordination clusters, with Ln = Dy (1), Gd(2) were synthesized with the Gd compound having a ground spin state of 17/2 and the Dy analogue showing SMM behavior in zero field.

In the burgeoning area of 3d-4f coordination clusters (CCs) for those showing Single Molecule Magnet (SMM) behavior it is becoming increasingly clear that the correct blend of 3d and 4f ions in conjunction with the resulting topology of the clusters are important factors governing this behavior.<sup>1</sup> For 3d/4f SMMs the magnetic behavior can show two slow relaxation regimes corresponding to the single 4f ion and to the exchange coupled 3d/4f processes as evidenced within the frequency window of routine ac susceptibility studies where, in contrast to 4f single ion systems,<sup>2,3</sup> these can obey an Arrhenius law with two linear dependences corresponding to the two relaxation pathways, as was shown for a Co<sup>II</sup>Dy<sup>III</sup> system.<sup>4</sup> Generally such systems can be treated within the coupled 3d/4f regime as giant spin systems. As such they show relatively low effective energy barriers to spin inversion ( $U_{\text{eff}}$ ) when compared with the very high barriers often predicted for single 4f ion systems.<sup>5</sup> However, this is compensated by a suppression of quantum tunneling effects, which are particularly complicated and prevalent for 4f single ions. Thus, for high spin 3d/4f systems it can be possible to observe and analyze the relaxation data within the usual frequency window of ac susceptibility measurements in zero applied dc field for both the single ion and exchange coupled cases.<sup>4</sup>

CCs combining highly anisotropic 4f ions such as Dy<sup>III</sup> with the quantum spin Cu<sup>II</sup> d<sup>9</sup> ion<sup>6</sup> have received less attention than other combinations, but amongst the relatively few examples of such SMMs,<sup>7</sup> the even rarer cases with high nuclearities above 10<sup>8-12,7</sup> have the advantage that the molecules possessing high spins and are well-separated within the crystal structure. Although these systems can show slow relaxation of the magnetization, as evidenced by frequency-dependent ac-susceptibilities, the maxima of the

characteristic out-of-phase signals are often shifted beyond the available frequency window.<sup>9,10</sup> Only rarely the SMM behaviour can be proved solely by ac measurements.<sup>7</sup>

We show here how a ligand engineering approach applied to a system with a favorable core spin-topology leads to Cu<sup>II</sup>/Dy<sup>III</sup> SMM. We took our previously reported Cu<sub>5</sub>Gd<sub>2</sub> CC, for which we were unable to isolate the Dy<sup>III</sup> analogue, as a starting point. This has a high  $S = 17/2$  ground spin state and is synthesized using the Schiff-base ligand H<sub>4</sub>L1 (Figure 3),<sup>13</sup> based on *o*-vanillin and tris(hydroxymethyl)aminoethane (tris). Given that one or even two hydroxyl groups of the tripodal alcohol unit may not be involved in coordination, but form inter- and intramolecular hydrogen-bonds to solvent molecules, neighbouring clusters or internal OH-groups,<sup>14-16</sup> we decided to replace one of the CH<sub>2</sub>OH alcohol groups with a CH<sub>3</sub> methyl unit to give the ligand H<sub>3</sub>L2 (Figure 3). This results in the cancellation of hydrogen-bonding involving this arm, allowing for a nuclearity expansion. Indeed, this approach has been used in Co<sup>II</sup>/III CCs, but led not only to cluster expansion but also a change in core motif.<sup>15,16</sup> In the compounds we report here this approach has been successfully applied to expanding the Cu<sub>5</sub>Ln<sub>2</sub> by the addition of two Cu<sub>2</sub> units to give a Cu<sub>9</sub>Ln<sub>2</sub> topology with the same core motif as in Cu<sub>5</sub>Gd<sub>2</sub> for both Ln = Gd<sup>III</sup> or Dy<sup>III</sup>, with the latter showing SMM behaviour.



**Figure 1.** Molecular structure of Cu<sub>9</sub>Dy<sub>2</sub> (organic H atoms omitted for clarity;  $\mu$ -bridging bonds highlighted in orange, benzene rings highlighted according coordination mode, see Scheme S1).

Compound  $[\text{Cu}_9\text{Dy}_2(\mu_3\text{-OH})_4(\mu_3\text{-Br})_2(\text{L}2)_2(\text{HL}2)_4(\text{Br})_2(\text{NO}_3)_2(\text{MeOH})_4] \cdot 6\text{MeOH}$  (**1**·6MeOH) crystallizes in the triclinic space group  $P\bar{1}$  with  $Z = 2$  (Figure 1). The central  $\text{Cu}^{\text{II}}$  ion, Cu(1), of this undecanuclear CC sits on an inversion center. The central core (Figure S1) is essentially the same as that of the previously reported  $\text{Cu}_5\text{Gd}_2$  cluster.<sup>13</sup> The  $\{\text{Cu}_5\text{Dy}_2\}$  unit is bridged by four  $\mu_3$ -hydroxides, O(1), O(1'), O(2) and O(2'), each of which bridge between two  $\text{Cu}^{\text{II}}$  and one  $\text{Dy}^{\text{III}}$  ion. Cu(1) provides the common vertex of two Cu-triangles, which are linked together by one  $\mu_3$ -bridging bromide ligand, Br(1) or Br(1'), albeit with rather long bond distances of between 2.8604(13) to 2.9627(13) Å.

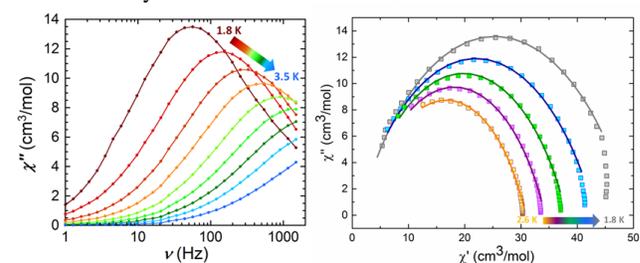
Cu(1) exhibits a 4+2 distorted octahedral coordination sphere with bromides on the elongated Jahn-Teller axis. The Cu(4) ions also have a J-T distorted octahedral coordination environment, but with one bromide Br(2) and one methanolate, O(8), in the axial positions. Cu(2) and Cu(3) have square-pyramidal coordination. Cu(5) has a square-planar ligand environment (Figure S2). The  $\text{Dy}^{\text{III}}$  ions are nine-coordinate.

The six Schiff-base ligands show three different coordination modes (Scheme S1 and Figure 1). Four of these are doubly deprotonated with the loss of the H-atoms on the phenol and one diol oxygen and bridge two or three metal ions, while the remaining two ligands are completely deprotonated and bridge four metal ions. It has been shown for Cu/Dy complexes with Schiff-base ligands based on *o*-vanillin can provide two pockets for metal ion coordination.<sup>17–21</sup> One pocket is formed by the phenoxo oxygen and the imine nitrogen, which in the current compound always occupied by a  $\text{Cu}^{\text{II}}$  ion, similarly to previously reported Cu/Ln complexes.<sup>9,17</sup> The other pocket defined by the phenoxo and the methoxy oxygens can incorporate a  $\text{Cu}^{\text{II}}$  or a  $\text{Dy}^{\text{III}}$  ion or remain vacant. One of the alcohol arms is always coordinated to one  $\text{Cu}^{\text{II}}$  ion assisting with the chelation of this metal ion in the first pocket as well as having the possibility to bridge to a second  $\text{Cu}^{\text{II}}$  ion, with or without the help of the second diol arm. The Cu-O and Cu-N bond lengths are between 1.891(6) and 2.086(5) Å, while the bond lengths on the Jahn-Teller-axis are slightly extended with 2.65 Å for Cu(4)-O(8). The static (dc) magnetic properties for both compounds were studied between 1.9 and 300 K under an applied field of 1000 Oe (Figure S3). The  $\chi_{\text{M}}T$  value of  $34.3 \text{ cm}^3\text{Kmol}^{-1}$  of **1**·6MeOH·4H<sub>2</sub>O at room temperature is in good agreement with what is expected for nine non-interacting  $\text{Cu}^{\text{II}}$  ( $S = 1/2$ ,  $g = 2$ ,  $C = 0.375 \text{ cm}^3\text{K/mol}$ ) and two  $\text{Dy}^{\text{III}}$  ( $S = 5/2$ ,  ${}^6\text{H}_{15/2}$ ,  $g = 4/3$ ,  $C = 14.17 \text{ cm}^3\text{K/mol}$ ) ions ( $31.7 \text{ cm}^3\text{K/mol}$ ). The  $\chi_{\text{M}}T$  value of  $18.9 \text{ cm}^3\text{Kmol}^{-1}$  for the isostructural  $\text{Gd}^{\text{III}}$  containing complex **2** is in good agreement ( $S = 7/2$ ,  ${}^8\text{S}_{7/2}$ ,  $g = 2$ ,  $C = 7.88 \text{ cm}^3\text{K/mol}$ ) with the expected value of  $19.09 \text{ cm}^3\text{K/mol}$ . On lowering the temperature, the  $\chi T$  product of **1** decreases until it reaches the minimum value of  $30.1 \text{ cm}^3\text{K/mol}$  at 26 K. For complex **2**·7H<sub>2</sub>O the  $\chi T$  product stays almost constant on lowering the temperature to 40 K. On further cooling, the  $\chi T$  values for both complexes continuously increase to reach a value of  $52.2 \text{ cm}^3\text{K/mol}$  at 1.9 K for **1** and  $32.7 \text{ cm}^3\text{K/mol}$  for **2**, respectively. This is in line with a ferrimagnetic spin topology amongst the metal centers.

For compound **2**, the magnetization shows a clear saturation above 3 T and the reduced (Figure S4) shows the superposition of the three isotherms on to one master curve, as expected for isotropic systems. The saturation value of  $17.05 \mu_{\text{B}}$  at 7 T and 2 K is much lower than the expected  $23.0 \mu_{\text{B}}$  for two  $\text{Gd}^{\text{III}}$  ( $S = 7/2$ ) and nine  $\text{Cu}^{\text{II}}$  ( $S = 1/2$ ) ions, which are uncoupled or completely ferromag-

netically coupled, suggesting that there is a degree of antiferromagnetic coupling. If we assume that there is a similar spin-orientation within the  $\text{Cu}_9\text{Gd}_2$  core (**2**) (Figure 3, S5) and therefore in the  $\text{Cu}_9\text{Dy}_2$  as in the previously reported  $\text{Cu}_5\text{Gd}_2$ <sup>13</sup> we expect ferromagnetic Cu-Dy interactions through double oxo-bridges<sup>22</sup> while the Cu-Cu interactions through  $\mu_3$ -Br ions are strongly antiferromagnetic.<sup>23</sup> The additional two copper dinuclear units on both sides of the core (Cu(4) and Cu(5) and symmetry equivalents) are antiferromagnetically coupled as suggested from their oxo-bridged angles of  $98.6(3)^\circ$  for Cu(4)-O(13)-Cu(5) and  $96.5(2)^\circ$  for Cu(4)-O(6)-Cu(5).<sup>24,25</sup> Within a giant spin model this leads to a predicted value of  $17.0 \mu_{\text{B}}$  for the magnetization and therefore a spin ground state of  $S = 17/2$ , in excellent agreement with the measured one ( $17.05 \mu_{\text{B}}$ ). For compound **1**, the magnetization measurements show no saturation up to 7 T for compound **1** (Figure S4). For the higher temperature isotherms, the values rapidly increase at low temperatures before following a more gradual linear increase without saturation.

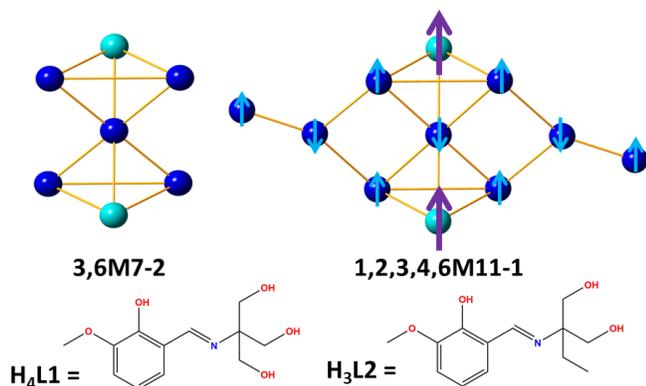
Ac susceptibility measurements performed on compound **1** display frequency-dependent peaks in the out-of-phase signals (Figure 2 and S6) even in the absence of an applied external field. This points to a lack of quantum tunneling in this frequency range, contrary to what is usually the case for Cu-Ln clusters.<sup>26,27</sup>



**Figure 2.** Frequency dependence of  $\chi_{\text{M}}''$  for  $\text{Cu}_9\text{Dy}_2$  (**1**) in a zero applied dc field in a range between 1.8 to 3.5 K (left) and Cole-Cole plot between 1.8 and 2.6 K; solid lines are fits of the experimental data (right).

The signals are temperature dependent between 1.8 and 2.6 K over the entire available frequency range. Above 2.8 K the peaks are shifted to higher frequencies and the maxima are beyond the available frequency window. The data between 1.8 - 2.6 K were used to extract the relaxation time as a function of temperature. The  $\ln(\tau)$  versus  $1/T$  points fit a linear curve, suggesting that an Orbach process is operative over the whole studied temperature and frequency range. A fit to the Arrhenius equation (Figure S7) gives  $U_{\text{eff}} = 16.1 \text{ K}$  and  $\tau_0 = 3.6 \cdot 10^{-7} \text{ s}$  ( $R = 0.99$ ). Cole-Cole plots of  $\chi_{\text{M}}''$  versus  $\chi_{\text{M}}'$  between 1.8 to 2.6 K (Figure 2) have semi-circular profiles, indicative of a single relaxation process. The plot was fitted with CC-Fit,<sup>28</sup> which uses a generalized Debye model.<sup>29</sup> The extracted parameters (see ESI) are similar to those reported for the  $\text{Cu}_8\text{Dy}_9$  complex.<sup>7</sup>

A topological analysis of the isostructural compounds **1** and **2**, taking the long Cu - Br bond distances into account, in line with the magnetic exchange pathways and spin topology, was performed using TOPOS software<sup>30</sup> (originally developed to describe MOFs) and adopting the NDK-m<sup>31</sup> symbolism for application to coordination clusters. This shows that the clusters can be represented as **1,2,3,4,6M11-1** (Figure 3). This appears to be the first example of this topology ever reported in 3d, 4f, or 3d/4f polynuclear coordination cluster chemistry. The fact that this core motif is a decorated version of that in the  $[\text{Cu}_5\text{Gd}_2]$ <sup>13</sup> compound (**3,6M7-2**) is easily verified by graphical screening.



**Figure 3.** Topological analysis of complex **2** (right) compared with the previously reported Cu<sub>5</sub>Gd<sub>2</sub> complex<sup>13</sup> (left) (Gd<sup>III</sup> ions turquoise, Cu<sup>II</sup> ions dark blue) and the spin-orientation of the metal centres in Cu<sub>9</sub>Gd<sub>2</sub> (**2**). The associated Schiff-base ligands are shown below.

Scrutinizing the molecular formula, the synthetic recipe and the organic ligands used to build these entities, it is clear that the presence of the CH<sub>3</sub> group in complex **1** in place of the OH group in the Cu<sub>5</sub>Gd<sub>2</sub> compound<sup>13</sup> favors the addition of two Cu<sub>2</sub> units resulting in the formation of the undecanuclear species as a result of deletion of H-bonding with adjacent or solvent molecules. Other modifications to the ligand offer further possibilities for structural tuning. We have successfully used a ligand modification approach to increase the nuclearity of the high-spin Cu<sub>5</sub>Gd<sub>2</sub> to give a Cu<sub>9</sub>Ln<sub>2</sub> system (Ln = Gd, Dy) whilst maintaining the same core topology and spin structure, as revealed from the study of Cu<sub>9</sub>Gd<sub>2</sub>. The Dy<sup>III</sup> analogue shows SMM behavior even in the absence of an applied field as revealed by ac susceptibility measurements.

## ASSOCIATED CONTENT

### Supporting Information

Crystallographic details, synthesis, magnetic data, topological analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

All authors have given approval to the final version of the manuscript.

### Funding Sources

DFG CFN and the Helmholtz Gemeinschaft POF STN.

### Notes

The authors declare no competing financial interests.

## ACKNOWLEDGMENT

We thank Abhishake Mondal and Valeriu Mereacre for collecting the magnetic data. I.A.K. thanks Amy-Jane Hutchings for her great help during this project.

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