Inorganic Chemistry

Communication

pubs.acs.org/IC

An Undecanuclear Ferrimagnetic Cu_9Dy_2 Single Molecule Magnet Achieved through Ligand Fine-Tuning

Irina A. Kühne,[†] George E. Kostakis,[‡,§] Christopher E. Anson,[†] and Annie K. Powell*[,†,#]

[†]Institut für Anorganische Chemie, Karlsruhe Institute of Technology (KIT), Engesserstrasse 15, D-76131 Karlsruhe, Germany
[‡]Department of Chemistry, School of Life Sciences, University of Sussex, Arundel Building 305, BN1 9QJ Sussex, U.K.
[§]Science and Educational Center of Physics of Noneqiliubrium Open Systems, Samara State Aerospace University (National Research University), Moskovskoye Shosse 34, Samara 443086, Russia
[#]Institute of Nanotechnology, KIT, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

S *Supporting Information*

ABSTRACT: We describe the concept of increasing the nuclearity of a previously reported high-spin Cu_5Gd_2 core using a "fine-tuning" ligand approach. Thus, two Cu_9Ln_2 coordination clusters, with Ln = Dy (**1**) and Gd (**2**), were synthesized with the Gd compound having a ground spin state of $^{17}/_2$ and the Dy analogue showing single-molecule-magnet 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 and the resulting topology of the clusters are important factors governing this behavior.[1] For 3d/4f SMMs, the magnetic behavior can show two slow relaxation regimes corresponding to the 4f single ion and to the exchange-coupled 3d/4f processes, as evidenced within the frequency window of routine alternating-current (ac) susceptibility studies. Here, in contrast to 4f single-ion systems,[2,3] these can obey an Arrhenius law, with two linear dependences corresponding to the two relaxation pathways, as was shown for a $Co^{II}{}_2Dy^{III}{}_2$ system.[4] 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_{eff}) compared with the very high barriers often predicted for 4f single-ion systems.[5] However, this is compensated for 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 a zero applied direct-current (dc) field for both the single-ion and exchange-coupled cases.[4]

CCs combining highly anisotropic 4f ions such as Dy^{III} with the quantum spin Cu^{II} d^9 ion[6] have received less attention than other combinations. Among the relatively few examples of such SMMs,[7−9] the ones with high nuclearities above ten[7,10−14] are even rarer. These have the advantage that the molecules possess high spins and are well separated within the crystal structure. Although these systems can show slow relaxation of 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.[11,12] Thus, only rarely can the SMM behavior be probed solely by ac measurments.[7]

We show here how a ligand engineering approach applied to a system with a favorable core spin topology leads to a Cu^{II}/Dy^{III} SMM. We took our previously reported Cu_5Gd_2 CC, for which we were unable to isolate the Dy^{III} analogue, as a starting point. This has a high $S = {}^{17}/_2$ ground spin state and is synthesized using the Schiff-base ligand H_4L1,[15] 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 can form inter- and intramolecular hydrogen bonds to solvent molecules, neighboring clusters, or internal OH groups,[16−18] we decided to replace one of the CH_2OH alcohol groups with a CH_3 methyl unit to give the ligand H_3L2. This results in the cancellation of hydrogen bonding involving this arm, allowing for a nuclearity expansion. Indeed, this approach has been used in $Co^{II,III}$ CCs but led not only to cluster expansion but also to a change in the core motif.[17,18] In the compounds we report here, this approach has been successfully applied to expanding Cu_5Ln_2 by the addition of two Cu_2 units to give a Cu_9Ln_2 topology with the same core motif as that in Cu_5Gd_2 for both Ln = Gd^{III} and Dy^{III}, with the latter showing SMM behavior.

Compound $[Cu_9Dy_2(\mu_3\text{-}OH)_4(\mu_3\text{-}Br)_2(L2)_2(HL2)_4(Br)_2(NO_3)_2(MeOH)_4]\cdot 6MeOH$ (**1**·6MeOH) was synthesized by mixing a ligand solution of H_3L2 (0.25 mmol) and triethylamine (1.0 mmol) with a solution of $CuBr_2$ (0.25 mmol) and $Dy(NO_3)_3\cdot 6H_2O$ (0.25 mmol) in 10.0 mL of methanol. **1**·6MeOH crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ (Figure 1).

The central Cu^{II} ion, Cu(1), of this undecanuclear CC sits on an inversion center. The basic core (Figure S1) is essentially the same as that of the previously reported Cu_5Gd_2 cluster.[15] The $\{Cu_5Dy_2\}$ unit is bridged by four μ_3-hydroxides, O(1), O(1′), O(2), and O(2′), each of which bridges between two Cu^{II} and one Dy^{III} ion. Cu(1) provides the common vertex of two Cu triangles, which are linked together by one μ_3-bridging bromide ligand, Br(1) or Br(1′), albeit with rather long bond distances of between 2.8604(13) and 2.9627(13) Å.

Cu(1) exhibits a 4 + 2 distorted octahedral coordination sphere with bromides on the elongated Jahn−Teller (JT) axis.

Received: March 2, 2016

DOI: 10.1021/acs.inorgchem.6b00490
Inorg. Chem. XXXX, XXX, XXX−XXX

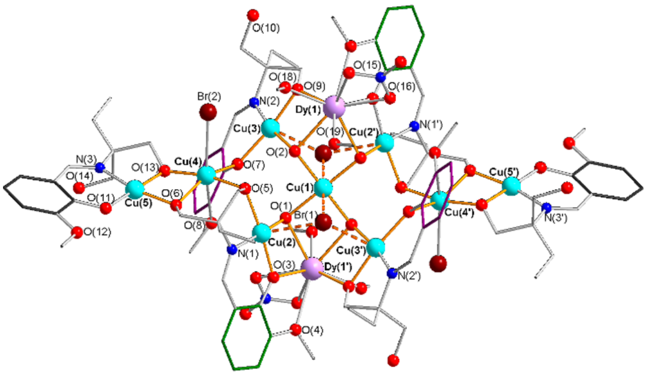

Figure 1. Molecular structure of Cu_9Dy_2 (organic H atoms omitted for clarity; μ-bridging bonds highlighted in orange, benzene rings highlighted according to coordination mode; see Figure S1).

The Cu(4) ions also have a JT distorted octahedral coordination environment but with one bromide, Br(2), and one methanol, 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 Dy^{III} ions are nine-coordinate.

The six Schiff-base ligands show three different coordination modes (Scheme S1). Four of these are doubly deprotonated with the loss of H atoms on the phenol and one diol O atom and bridge two or three metal ions, while the remaining two ligands are completely deprotonated and bridge four metal ions. This has been shown for Cu/Dy complexes with Schiff-base ligands based on *o*-vanillin providing two pockets for metal-ion coordination.[19−23] One pocket is formed by the phenoxo O atom and the imine N atom, which in the current compound is always occupied by a Cu^{II} ion, similar to previously reported Cu/Ln complexes.[11,19] The other pocket, defined by the phenoxy and methoxy O atoms, can incorporate a Cu^{II} or Dy^{III} ion or remain vacant. One of the alcohol arms is always coordinated to one Cu^{II} ion, assisting with chelation of this metal ion in the first pocket as well as having the possibility of bridging to a second Cu^{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 JT axis are extended with 2.65 Å for Cu(4)−O(8).

The static (dc) magnetic properties for both compounds with the formulas $\mathbf{1}\cdot 6MeOH\cdot 4H_2O$ and $\mathbf{2}\cdot 7H_2O$ (formulas consistent with C, H, and N analyses on fresh samples) were studied between 1.9 and 300 K under an applied field of 1000 Oe (Figure S3). The $\chi_M T$ value of 34.3 $cm^3\cdot K/mol$ of $\mathbf{1}\cdot 6MeOH\cdot 4H_2O$ at room temperature is in good agreement with what is expected for nine noninteracting Cu^{II} ($S = {}^1/_2$, $g = 2$, $C = 0.375$ $cm^3\cdot K/mol$) and two Dy^{III} ($S = {}^5/_2$, ${}^6H_{15/2}$, $g = {}^4/_3$, $C = 14.17$ $cm^3\cdot K/mol$) ions (31.7 $cm^3\cdot K/mol$). The $\chi_M T$ value of 18.9 $cm^3\cdot K/mol$ for the isostructural Gd^{III}-containing compound $\mathbf{2}\cdot 7H_2O$ is in good agreement ($S = {}^7/_2$, ${}^8S_{7/2}$, $g = 2$, $C = 7.88$ $cm^3\cdot K/mol$) with the expected value of 19.09 $cm^3\cdot K/mol$. Upon lowering the temperature, the χT product of **1** decreases until it reaches the minimum value of 30.1 $cm^3\cdot K/mol$ at 26 K. For compound $\mathbf{2}\cdot 7H_2O$, the χT product stays almost constant upon lowering of the temperature to 40 K. Upon further cooling, the χT values for both compounds continuously increase to reach a value of 52.2 $cm^3\cdot K/mol$ at 1.9 K for **1** and 32.7 $cm^3\cdot K/mol$ for **2**. This is in line with a ferrimagnetic spin topology among the metal centers.

For compound **2**, the magnetization shows a clear saturation above 3 T and the reduced magnetization (Figure S4) shows superposition of the three isotherms onto one master curve, as expected for isotropic systems. The saturation value of 17.05 μ_B at 7 T and 2 K is much lower than the expected 23.0 μ_B for two Gd^{III} ($S = {}^7/_2$) and nine Cu^{II} ($S = {}^1/_2$) ions, which are uncoupled or completely ferromagnetically coupled, suggesting that there is a degree of antiferromagnetic coupling. If we assume that there is a similar spin orientation within the Cu_9Gd_2 core (**2**; Figures 3 and S5), and therefore in Cu_9Dy_2, as in the previously reported Cu_5Gd_2,[15] we expect ferromagnetic Cu−Dy interactions through double oxo bridges,[24] while the Cu−Cu interactions through μ_3-Br ions are strongly antiferromagnetic.[25] 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)° for Cu(4)−O(13)−Cu(5) and 96.5(2)° for Cu(4)−O(6)−Cu(5).[26,27] Within a giant spin model, this leads to a predicted value of 17.0 μ_B for the magnetization and therefore a spin ground state of $S = {}^{17}/_2$, in excellent agreement with the measured one (17.05 μ_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.

The ac susceptibility measurements performed on compound **1** display frequency-dependent peaks in the out-of-phase signals (Figures 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.[28,29]

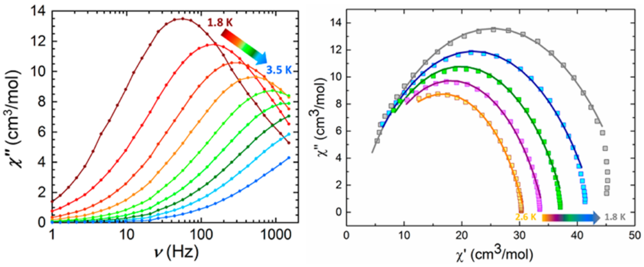

Figure 2. Frequency dependence of χ_M'' for Cu_9Dy_2 (**1**) in a zero applied dc field in the range between 1.8 and 3.5 K (left) and Cole−Cole plot between 1.8 and 2.6 K. The solid lines are fits of the experimental data (right).

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 and 2.6 K were used to extract the relaxation time as a function of the temperature. The ln(τ) 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 $U_{eff} = 16.1$ K and $\tau_0 = 3.6 \times 10^{-7}$ s ($R = 0.99$). Cole-Cole plots of χ_M' versus χ_M'' between 1.8 and 2.6 K (Figure 2) have semicircular profiles, indicative of a single relaxation process. The plot was fitted with CC-Fit,[28] which uses a generalized Debye model.[30,31] The extracted parameters (see the Supporting Information) are similar to those reported for the Cu_8Dy_9 complex.[9]

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[32] (originally developed to describe metal-organic frameworks) and adopting the *N*Dk-*m*[33] symbolism for application to CCs. 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 CC chemistry. The fact that this core motif is a decorated version of that in the $[Cu_5Gd_2]$[15] complex (**3,6M7-2**) is easily verified by graphical screening. When the molecular formula, the synthetic recipe, and the organic ligands used to build these entities are scrutinized, it is clear that the presence of the CH_3 group in complex **1** in place of the OH group in the Cu_5Gd_2 complex[15] favors the addition of two Cu_2 units, resulting in the formation of the undecanuclear species as a result of the deletion of hydrogen bonding with adjacent or solvent molecules. Other modifications to the ligand offer further possibilities for structural tuning.

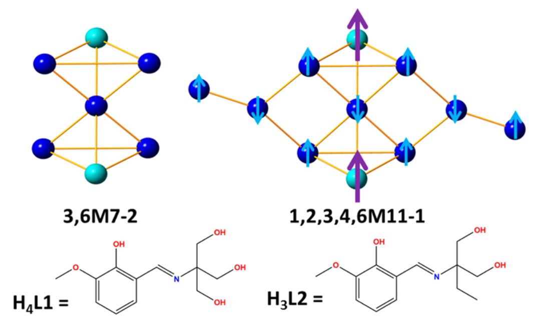

Figure 3. Topological analysis of complex **2** (right) compared with the previously reported Cu_5Gd_2 complex[13] (left) (Gd^{III} ions, turquoise; Cu^{II} ions, dark blue) and spin orientation of the metal centers in Cu_9Gd_2 (**2**). The associated Schiff-base ligands are shown below.

We have successfully used a ligand modification approach to increase the nuclearity of the high-spin Cu_5Gd_2 to give a Cu_9Ln_2 system (Ln = Gd, Dy) while maintaining the same core topology and spin structure, as revealed from the study of Cu_9Gd_2. The Dy^{III} analogue shows SMM behavior even in the absence of an applied field, as revealed by the ac susceptibility measurements.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00490.

Synthesis, magnetic data, and topological analysis (PDF)
Crystallographic details in CIF format (CIF)
Crystallographic details in CIF format (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: annie.powell@kit.edu. Tel: +49 721 608 42135.

Author Contributions

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

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

DFG CFN and the Helmholtz Gemeinschaft POF STN provided funding. 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.

■ REFERENCES

(1) Kostakis, G. E.; Powell, A. K. *Chem. - Eur. J.* **2010**, *16*, 7983.
(2) Rechkemmer, Y.; Fischer, J. E.; Marx, R.; Dörfel, M.; Neugebauer, P.; Horvath, S.; Gysler, M.; Brock-Nannestad, T.; Frey, W.; Reid, M. F.; Van Slageren, J. *J. Am. Chem. Soc.* **2015**, *137*, 13114.
(3) Pedersen, K. S.; Dreiser, J.; Weihe, H.; Sibille, R.; Johannesen, H. V.; Sørensen, M. A.; Nielsen, B. E.; Sigrist, M.; Mutka, H.; Rols, S.; Bendix, J.; Piligkos, S. *Inorg. Chem.* **2015**, *54*, 7600.
(4) Mondal, K. C.; Sundt, A.; Lan, Y.; Kostakis, G. E.; Waldmann, O.; Ungur, L.; Chibotaru, L. F.; Anson, C. E.; Powell, A. K. *Angew. Chem., Int. Ed.* **2012**, *51*, 7550.
(5) Rinehart, J. D.; Long, J. R. *Chem. Sci.* **2011**, *2*, 2078.
(6) Schnack, J. *Condensed Matter* **2015**, 1−8.
(7) Liu, J.-L.; Lin, W.-Q.; Chen, Y.-C.; Gómez-Coca, S.; Aravena, D.; Ruiz, E.; Leng, J.-D.; Tong, M.-L. *Chem. - Eur. J.* **2013**, *19*, 17567.
(8) Costes, J.-P.; Auchel, M.; Dahan, F.; Peyrou, V.; Shova, S.; Wernsdorfer, W. *Inorg. Chem.* **2006**, *45*, 1924.
(9) Aronica, C.; Chastanet, G.; Pilet, G.; Le Guennic, B.; Robert, V.; Wernsdorfer, W.; Luneau, D. *Inorg. Chem.* **2007**, *46*, 6108.
(10) Dermitzaki, D.; Raptopoulou, C. P.; Psycharis, V.; Escuer, A.; Perlepes, S. P.; Stamatatos, T. C. *Inorg. Chem.* **2015**, *54*, 7555.
(11) Iasco, O.; Novitchi, G.; Jeanneau, E.; Luneau, D. *Inorg. Chem.* **2013**, *52*, 8723.
(12) Leng, J.-D.; Liu, J.-L.; Tong, M.-L. *Chem. Commun.* **2012**, *48*, 5286.
(13) Iasco, O.; Novitchi, G.; Jeanneau, E.; Wernsdorfer, W.; Luneau, D. *Inorg. Chem.* **2011**, *50*, 7373.
(14) Baskar, V.; Gopal, K.; Helliwell, M.; Tuna, F.; Wernsdorfer, W.; Winpenny, R. E. P. *Dalton Trans.* **2010**, *39*, 4747.
(15) Wu, G.; Hewitt, I. J.; Mameri, S.; Lan, Y.; Clérac, R.; Anson, C. E.; Qiu, S.; Powell, A. K. *Inorg. Chem.* **2007**, *46*, 7229.
(16) Zhou, Q.; Yang, F.; Liu, D.; Peng, Y.; Li, G.; Shi, Z.; Feng, S. *Dalton Trans.* **2013**, *42*, 1039.
(17) Jia, Z.-Q.; Sun, X.-J.; Hu, L.-L.; Tao, J.; Huang, R.-B.; Zheng, L.-S. *Dalton Trans.* **2009**, 6364.
(18) Zhou, H.; Chen, Y.-Y.; Yuan, A.-H.; Shen, X.-P. *Inorg. Chem. Commun.* **2008**, *11*, 363.
(19) Kühne, I. A.; Magnani, N.; Mereacre, V.; Wernsdorfer, W.; Anson, C. E.; Powell, A. K. *Chem. Commun.* **2014**, *50*, 1882.
(20) Kajiwara, T.; Nakano, M.; Takahashi, K.; Takaishi, S.; Yamashita, M. *Chem. - Eur. J.* **2011**, *17*, 196.
(21) Xue, S.; Guo, Y. N.; Zhao, L.; Zhang, H.; Tang, J. *Inorg. Chem.* **2014**, *53*, 8165.
(22) Zhang, P.; Zhang, L.; Lin, S.; Tang, J. *Inorg. Chem.* **2013**, *52*, 6595.
(23) Sieklucka, B.; Podgajny, R.; Pinkowicz, D.; Nowicka, B.; Korzeniak, T.; Bałanda, M.; Wasiutyński, T.; Pełka, R.; Makarewicz, M.; Czapla, M.; Rams, M.; Gaweł, B.; Łasocha, W. *CrystEngComm* **2009**, *11*, 2032.
(24) Bencini, A.; Benelli, C.; Caneschi, A.; Carlin, R. L.; Dei, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1985**, *107*, 8128.
(25) Laborda, S.; Clerac, R.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2004**, *43*, 5931.
(26) Merz, L.; Haase, W. *J. Chem. Soc., Dalton Trans.* **1980**, *74*, 875.
(27) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, J. D.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.
(28) Maity, M.; Majee, M. C.; Kundu, S.; Samanta, S. K.; Sañudo, E. C.; Ghosh, S.; Chaudhury, M. *Inorg. Chem.* **2015**, *54*, 9715.
(29) Wen, H.-R.; Bao, J.; Liu, S.-J.; Liu, C.-M.; Zhang, C.-W.; Tang, Y.-Z. *Dalton Trans.* **2015**, *44*, 11191.
(30) Chilton, N. F. CC-Fit, http://www.nfchilton.com/cc-fit.html.
(31) Guo, Y.-N.; Xu, G.-F.; Guo, Y.; Tang, J. *Dalton Trans.* **2011**, *40*, 9953.
(32) Blatov, V. A.; Shevchenko, A. P.; Proserpio, D. M. *Cryst. Growth Des.* **2014**, *14*, 3576.
(33) Kostakis, G. E.; Blatov, V. A.; Proserpio, D. M. *Dalton Trans.* **2012**, *41*, 4634.