Inorg. Chem. **2007**, *46*, 7229–7231

Inorganic Chemistry
Communication

Bifunctional Ligand Approach for Constructing 3d–4f Heterometallic Clusters

Gang Wu,†,‡ Ian J. Hewitt,†,‡ Samir Mameri,‡ Yanhua Lan,‡ Rodolphe Clérac,§ Christopher E. Anson,‡ Shilun Qiu,*,† and Annie K. Powell*,‡

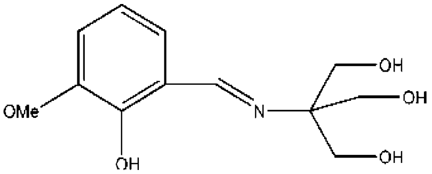
Institut für Anorganische Chemie der Universität Karlsruhe, Engesserstrasse Geb. 30.45, D-76128 Karlsruhe, Germany, State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China, and Université Bordeaux 1, CNRS, Centre de Recherche Paul Pascal, UPR8641, 115 avenue du Dr. Albert Schweitzer, 33600 Pessac, France

Received February 14, 2007

Using a predesigned Schiff-base tripodal ligand, a heptanuclear Cu^{II}–Gd^{III} cluster with a spin ground state of $S = {}^{17}/_{2}$ has been synthesized.

The design and synthesis of high-nuclearity clusters that can behave as single-molecule magnets (SMMs) is an area of high activity relevant to magnetochemistry and coordination chemistry.[1] Since the discovery of the first SMM Mn12,[1e−g] several homo-[1,2] and heterometallic[3] clusters have been described that display slow relaxation of the magnetization, which is usually regarded as an indication of possible SMM behavior. One way of combining the high-spin ground state and uniaxial anisotropy properties required for SMM behavior is to synthesize heterometallic clusters, such as 3d−4f aggregates.[3a−d] This synthetic strategy has also led to the discovery of many beautiful and interesting clusters that although they do not display SMM properties provide a valuable insight into promising future synthetic directions.

Scheme 1



We present here a means of combining 3d and 4f centers using bifunctional ligands. Recognizing that Schiff-base ligands[4] are easy to tailor and that tripodal ligand groups[5] are a good way of connecting metal centers together, we decided to combine both groups in the ligand 2-{[(2-hydroxy-3-methoxyphenyl)methylene]amino}-2-(hydroxymethyl)-1,3-propanediol (H_4L; Scheme 1). This can be isolated in a quantitative yield by mixing methanolic solutions of *o*-vanillin and tris(hydroxymethyl)aminomethane.[6] This type of ligand has previously been used to prepare 3d homonuclear clusters.[6,7]

Herein we report the synthesis and magnetic property of a novel 3d−4f heteronuclear cluster $[Gd_2Cu_5(OH)_4(Br)_2(H_2L)_2(H_3L)_2(NO_3)_2(OH_2)_4](NO_3)_{1.78}(Br)_{0.22}\cdot 7H_2O$ (**1**), which has a spin ground state of $S = {}^{17}/_{2}$.

---

* To whom correspondence should be addressed. E-mail: sqiu@mail.jlu.edu.cn (S.Q.), powell@chemie.uni-karlsruhe.de (A.K.P.). Fax: (+49) 721-608-8142.

† Jilin University.

‡ Institut für Anorganische Chemie der Universität Karlsruhe.

§ Centre de Recherche Paul Pascal.

(1) (a) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, 141. (b) Christou, G.; Gatteschi, D.; Hendrickson, D. N.; Sessoli, R. *MRS Bull.* **2000**, *25*, 66. (c) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268. (d) Cadiou, C.; Murrie, M.; Paulsen, C.; Villar, V.; Wernsdorfer, W.; Winpenny, W. E. P. *Chem. Commun.* **2001**, 2666. (e) Lis, T. *Acta. Crystallogr.* **1980**, *B36*, 2042. (f) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Barra, A. L.; Brunel, L. C.; Guillot, M. *J. Am. Chem. Soc.* **1991**, *113*, 5873. (g) Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S. Y.; Vicent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804.

(2) (a) Tasiopoulos, A. T.; Vinslava, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2117. (b) Soler, M.; Wernsdorfer, W.; Folting, K.; Pink, M.; Christou, G. *J. Am. Chem. Soc.* **2004**, *126*, 2156. (c) Barra, A. L.; Debrunner, P.; Gatteschi, D.; Schula, C. E.; Sessoli, R. *Europhys. Lett.* **1996**, *35*, 133. (d) Castro, S. L.; Sun, Z. M.; Bollinger, J. C.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1995**, 2517.

(3) (a) Osa, S.; Kido, T.; Matsumoto, N.; Re, N.; Pochaba, A.; Mrozinski, J. *J. Am. Chem. Soc.* **2004**, *126*, 420. (b) Zaleski, C. M.; Depperman, E. C.; Kampf, J. W.; Kirk, M. L.; Pecoraro, V. L. *Angew. Chem.* **2004**, *43*, 3912. (c) Mishra, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *J. Am. Chem. Soc.* **2004**, *126*, 15648. (d) Aronica, C.; Pilet, G.; Chastanet, G.; Wernsdorfer, W.; Jacquot, J. S.; Luneau, D. *Angew. Chem.* **2006**, *118*, 4775. (e) Oshio, H.; Nihei, M.; Koizumi, S.; Shiga, T.; Nojiri, H.; Nakano, M.; Shirakawa, N.; Akatsu, M. *J. Am. Chem. Soc.* **2005**, *127*, 4568. (f) Yang, C. I.; Tsai, H. L.; Lee, G. H.; Wur, C. S.; Yang, S. F. *Chem. Lett.* **2005**, *34*, 288.

(4) (a) Gavilova, A. L.; Bosnich, B. *Chem. Rev.* **2004**, 349. (b) Cozzi, P. G. *Chem. Soc. Rev.* **2004**, *33*, 410.

(5) (a) Waldmann, O.; Koch, R.; Schromm, S.; Schulein, J.; Muller, P.; Bernt, I.; Saalfrank, R. W.; Hampel, F.; Balthes, E. *Inorg. Chem.* **2001**, *40*, 2986. (b) Brechin, E. K.; Soler, M.; Christou, G.; Helliwell, M.; Teat, S. J.; Wernsdorfer, W. *Chem. Commun.* **2003**, 1276. (c) Rajaraman, G.; Murugesu, M.; Sanudo, E. C.; Soler, M.; Wernsdorfer, W.; Helliwell, M.; Muryn, C.; Raftery, J.; Teat, S. J.; Christou, G.; Brechin, E. K. *J. Am. Chem. Soc.* **2004**, *126*, 15445. (d) Murugesu, M.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 892.

(6) Sreenivasulu, R.; Sreeramulu, J. *Acta Cienc. Indica, Chem.* **2004**, *30* (3), 181.

10.1021/ic070296a CCC: $37.00

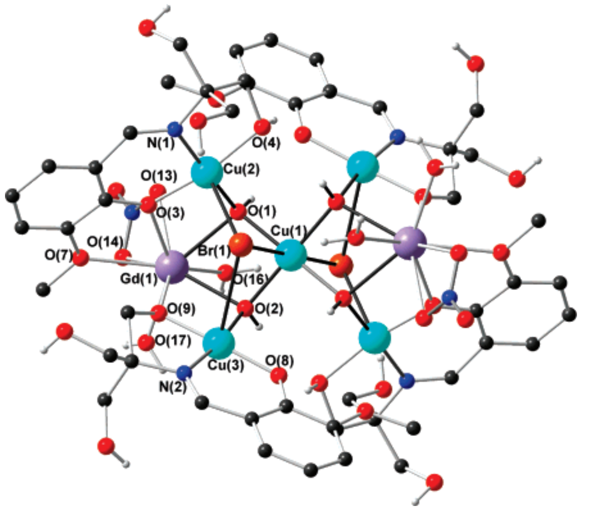


Figure 1. Molecular structure of the Cu_5Gd_2 aggregate in **1**. The C−H hydrogen atoms have been omitted for clarity.

Compound **1** was synthesized by slow evaporation of a methanolic solution of $CuBr_2 \cdot H_2O$, H_4L, and $Gd(NO_3)_3 \cdot 5H_2O$ in the presence of tetrabutylammonium hydroxide (TBA).[8]

The heptanuclear aggregate in **1** (Figure 1) is centrosymmetric, with Cu(1) situated on a crystal inversion center.[9]

The metal centers are linked together by four μ_3-OH ligands, each of which bridges between two Cu centers and a Gd, with Cu−O = 1.959−1.995 Å and Gd−O = 2.459 and 2.467 Å. Cu(1) has a 4 + 2 distorted octahedral coordination sphere, Cu(2) and Cu(3) have square-pyramidal geometries, while Gd(1) is nine-coordinate. There are two μ_3-Br ligands, which occupy axial sites on the Cu centers and bridge between three Cu atoms with Cu−Br = 2.826−3.139 Å. In addition to the strict inversion symmetry, the $\{Cu_5Gd_2(\mu_3\text{-OH})_4(\mu_3\text{-Br})_2\}$ core also has a pseudo-mirror-plane containing Cu(1), the Gd atoms, and the bromide ligands.

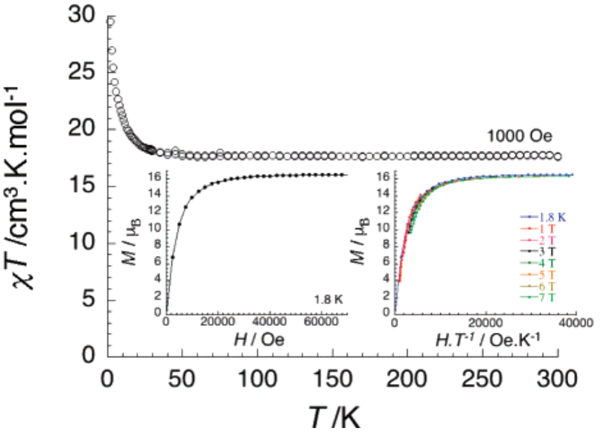


Figure 2. Temperature dependence of the χT product at 1000 Oe (with $\chi = M/H$) and magnetization measurements at 1.8 K (left inset) and presented as a reduced magnetization plot (M vs H/T, right inset) for **1**.

Each of the four outer coppers, Cu(2) and Cu(3) and equivalents, are chelated by the deprotonated phenol O, the imino N, and an ethanolic O of a Schiff-base ligand. In the ligand chelating Cu(2), the latter oxygen [O(4)] still carries its proton, with the phenoxo oxygen O(3) bridging to Gd(1), whereas in the ligand chelating Cu(3), the ethanolic oxygen O(9) is deprotonated and bridges to Gd(1). The coordination sphere of Gd(1) is completed by a chelating nitrate, an O atom from the methoxy group of the H_4L (in its H_3L version), and two aqua ligands. Thus, the ligand provides differing coordination sites attractive to the relatively soft Cu^{II} and hard Gd^{III} ions as well as bridging from phenol and alcohol O atoms. There are no real pathways for intermolecular magnetic exchange because any dangling O atoms from the ligands form intramolecular H bonds or H bonds to counterions apart from one intermolecular H bond from a dangling O in one molecule to the next for which the magnetic pathway would involve going through a total of two Cu−N bonds, six saturated C−O or C−C single bonds, plus the H bond.

Magnetic measurements were performed on a polycrystalline sample of **1**.[10] Between room temperature and 50 K, the χT product (Figure 2) is roughly constant at 17.8 $cm^3 \cdot K/mol$. This value is in good agreement with the expected value (17.625 $cm^3 \cdot K/mol$) for the presence of two Gd^{III} ($S = {}^7/_2$ with $C = 7.875$ $cm^3 \cdot K/mol$ for $g = 2$)[11] ions and five Cu^{II} ions ($S = {}^1/_2$ spin with $C = 0.375$ $cm^3 \cdot K/mol$). When the temperature is decreased below 50 K, the χT product at 1000 Oe continuously increases to reach 29.6 $cm^3 \cdot K/mol$ at 1.8 K, indicating the presence of ferromagnetic interactions in the complex.

---

(7) (a) Rustagi, S. C.; Rao, G. N. *Indian J. Chem.* **1975**, *13* (7), 702. (b) Asgedom, G.; Sreedhara, A.; Rao, C. P. *Polyhedron* **1995**, *14*, 1873. (c) Dey, M.; Rao, C. P.; Saarenketo, P. K.; Rissanen, K.; Kolehmainen, E. *Eur. J. Inorg. Chem.* **2002**, *8*, 2207. (d) Dey, M.; Rao, C. P.; Saarenketo, P. K.; Rissanen, K. *Inorg. Chem. Commun.* **2002**, *5* (11), 924.

(8) Synthesis of compound **1**: Slow evaporation at room temperature of a methanolic solution (15 mL) of $CuBr_2 \cdot H_2O$ (0.112 g, 0.5 mmol), H_4L (0.128 g, 0.5 mmol), and $Gd(NO_3)_3 \cdot 5H_2O$ (0.069 g, 0.2 mmol) in the presence of TBA (1.297 g, 0.5 mmol; 40% methanol solution) gave green plates of **1** after 1 week (0.09 g, 0.04 mmol, ca. 40% based on Cu). Anal. Calcd for $Cu_5Gd_2C_{48}H_{90}O_{43.34}N_{6.78}Br_{2.22}$ (2325.22): C, 24.77; H, 3.44; N, 4.21. Found: C, 24.9; H, 3.6; N, 4.3.

(9) Crystal structure of **1**: $C_{48}H_{88}Br_{2.22}Cu_5Gd_2N_{7.78}O_{46.34}$, $a = 11.6809(10)$ Å, $b = 12.5918(10)$ Å, $c = 15.1061(13)$ Å, $\alpha = 104.569(7)°$, $\beta = 99.987(7)°$, $\gamma = 112.359(6)°$, $V = 1896.7(3)$ Å^3, triclinic, $P\bar{1}$, $Z = 1$, $T = 150$ K, $F(000) = 1152$, $D_c = 2.036$ g cm^{-3}, μ(Mo Kα) = 4.374 mm^{-1}; green block 0.15 × 0.12 × 0.09 mm; 13 592 data measured, 7133 unique ($R_{int} = 0.0429$), 539 parameters refined to wR2 = 0.1450, $S = 1.048$ (all data), and R1 = 0.0535 [6278 with $I > 2\sigma(I)$], largest peak/hole in the final difference map +1.24/−3.16 e Å^{-3} [the hole is near Gd(1)]. The counteranion was a disordered superposition of bromide (11%) and nitrate (two orientations, 48 and 41%). Geometrical restraints for the nitrates and similarity restraints for the thermal parameters of the Br and N atoms allowed successful refinement. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 637154. Copies of the data can be obtained, free of charge, upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.: http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, e-mail data_request@ccdc.cam.ac.uk, or fax +44 1223 336033.

(10) The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for direct current applied fields ranging from −7 to +7 T. Measurements were performed on a polycrystalline sample of 8.5 mg. M vs H measurements have been performed at 100 K to check for the presence of ferromagnetic impurities that have been found to be absent. The magnetic data were corrected for the sample holder and the diamagnetic contribution.

(11) Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369−2387.

The magnetization measurements at 1.85 K (left inset in Figure 2) performed as a function of the field show a clear saturation above 4 T indicative (i) of an absence of field-induced population of the excited states below 7 T (i.e., excited states are relatively far away in energy above the ground state) and also (ii) of a low magnetic anisotropy. This latter conclusion is confirmed by the M vs H/T plot, where the data can all be superposed on a single master curve, as expected for isotropic systems (right inset in Figure 2). The saturation of M at 16.5 μ_B is lower than that expected (19 μ_B) for two Gd^{III} ($S = {}^7/_2$) ions and five $S = {}^1/_2$ Cu^{II} ions, which are uncoupled or completely ferromagnetically coupled. This suggests that even if ferromagnetic interactions are present, some of the centers are necessarily antiferromagnetically coupled in such a way that the applied magnetic field is not able to align all of the spins parallel to populate the $S = {}^{19}/_2$ excited state. Because the Cu−Gd interaction through double O bridges is nearly always ferromagnetic,[12] this behavior suggests that the Cu−Cu interaction through O/Br bridges is strongly antiferromagnetic, as has been observed previously.[13] In order to have a configuration compatible with the magnetization saturation at 16.5 μ_B, we must assume that the $Cu_2-Cu_{central}-Cu_2$ central motif of **1** possesses an antiferromagnetic arrangement with the central Cu^{II} $S = {}^1/_2$ spin in the opposite sense of the other Cu^{II} spins, as shown in Figure 3. Therefore, considering the presence of Cu−Gd ferromagnetic interactions, the resulting spin ground state of this system is $S = {}^{17}/_2$. The saturation value of the magnetization should be thus close to 17 μ_B, in good agreement with the experimental value. Attempts to simulate the magnetic susceptibility[14] by reducing the six different pathways of interaction to only two, J_{Cu-Cu} (mediated by an O/Br bridge) and J_{Gd-Cu} (mediated by a double O bridge), leads to multiple solutions because of the featureless χT vs T and M vs H/T experimental data. It is worth noting that the good simulations always gave large J_{Cu-Cu} values on the order of −100 K and small J_{Cu-Gd} values close to +1 K. As expected for isotropic systems, the magnetic properties of this compound reveal a complete absence of magnetization slow relaxation, i.e., SMM behavior, as confirmed by the lack of an out-of-phase alternating current signal or hysteresis effects on the M vs H data.

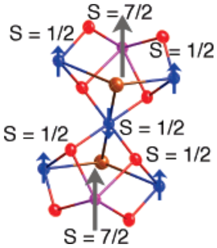


Figure 3. $Gd_2Cu_5O_8Br_2$ core structure of **1** highlighting the local spin arrangement of the ground state.

In summary, a new heptanuclear $Cu^{II}-Gd^{III}$ complex has been successfully synthesized using a predesigned Schiff-base tripodal ligand. Magnetic measurements reveal that this complex has an isotropic spin ground state of $S = {}^{17}/_2$. This synthetic method provides an entry to a systematic study using different combinations of 3d and 4f metals. In addition to the introduction of anisotropy in this way, secondary properties such as luminescence could be incorporated in the final materials.

Acknowledgment. This work was supported by MAGMANet (Grant NMP3-CT-2005-515767), the DAAD, Bordeaux 1 University, the CNRS, the Region Aquitaine, the French Ministries of Foreign Affairs and of Research, the National Nature Science Foundation of China (Grants 29873017, 20273026, and 20101004) and the State Basic Research Project (Grant G2000077507).

Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC070296A

---

(12) (a) Bencini, A.; Benelli, C.; Caneschi, A.; Carlin, R. L.; Day, A.; Gatteschi, D. *J. Am. Chem. Soc*. **1985**, *107*, 8128. (b) Bencini, A.; Benelli, C.; Caneschi, A.; Day, A.; Gatteschi, D. *Inorg. Chem.* **1986**, *25*, 572. (c) Benelli, C.; Caneschi, A.; Gatteschi, D.; Guillou, O.; Pardi, L. *Inorg. Chem*. **1990**, *29*, 1750.

(13) Laborda, S.; Clérac, R.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2004**, *43*, 5931.

(14) Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *J. Comput. Chem.* **2001**, *22*, 985.