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· Communication

Structure and Magnetic Properties of a Giant Cu$_{44}$^{II} Aggregate Which Packs with a Zeotypic Superstructure

Muralee Murugesu,[†] Rodolphe Clérac,[‡] Christopher E. Anson,[†] and Annie K. Powell*,[†]

Institut für Anorganische Chemie der Universität Karlsruhe, Engesserstrasse Geb. 30-45, D-76128 Karlsruhe, Germany, and Centre de Recherche Paul Pascal, CNRS UPR 8641, 115 Avenue Dr. A. Schweitzer, 33600 Pessac, France

Reaction of Cu(II) and the aminopolycarboxylate nitrilotripropionic acid (H$_3$ntp) in water leads to the formation of [Cu$_{44}$(μ_8-Br)$_2$-(μ_3-OH)$_{36}$(μ-OH)$_4$(ntp)$_{12}$Br$_8$(OH$_2$)$_{28}$]Br$_2$·81H$_2$O. The Cu$_{44}$ aggregates have a central inorganic core corresponding to [Cu$_{24}$(μ_8-Br)$_2$-(μ_3-OH)$_{24}$(μ-OH)$_8$]$^{14+}$ anchored on two bromide anions, and this is encased in a shell of Cu(II)/ligand units. The aggregates pack into a distorted tetragonal array with a very open structure containing large amounts of water of crystallization. The magnetic properties have been studied and, while complicated by the presence of low-lying excited states, indicate that the individual clusters have nonzero spin ground states.

The synthesis and crystallization of high-nuclearity, magnetically coupled transition metal aggregates is currently a major focus of research in the area of nanoscale materials, representing a bottom-up approach to the production of such systems and offering the possibility of creating ordered arrays, or superstructures, with secondary structural or physical properties. In general, this approach requires that specific conditions are hit upon so that the components self-assemble to give the aggregates and subsequent superstructure. However, as more examples become available it is possible to identify certain structural motifs and certain synthons which can help in the assembly of the systems. We have recently been exploring some Cu^{II} systems using polydentate aminocarboxylic acid chelating ligands (L) to trap intermediate species of general formula {M$_x$L$_n$(O)$_y$(OR)$_z$-(HOR)$_p$}$^{\pm b}$ from water or alcohol solutions to give aggregates where the Cu^{II} centers are linked through a mixture of solvent-derived and carboxylate bridges.[1] In the case of the Cu$_{36}$ system we recently reported,[1f] which forms in methanol, we found that the aggregate was centered on a {KCl$_6$}$^{5-}$ scaffold and conjectured that anionic templates could be useful in the stabilization of such frameworks as has been observed in a number of supramolecular anion templated systems based on simpler synthons.[2] Here we report on an

Figure 1. Structure of the Cu$_{44}$ aggregate **1**.
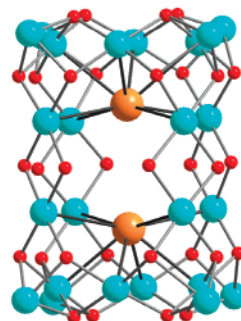
Figure 2. The inorganic [Cu$_{24}$(μ_8-Br)$_2$(μ_3-OH)$_{24}$(μ-OH)$_8$]$^{14+}$ core in **1**.

even larger Cu^{II} aggregate with 44 copper centers featuring two central bromide templates and a zeotypic superstructure.

* To whom correspondence should be addressed. E-mail: powell@chemie.uni-karlsruhe.de.
† Institut für Anorganische Chemie der Universität Karlsruhe.
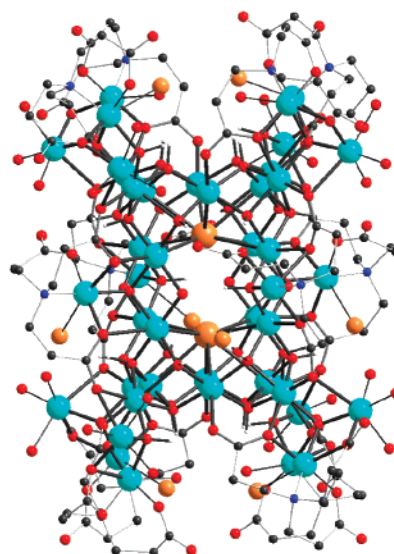‡ Centre de Recherche Paul Pascal.

(1) (a) Murugesu, M.; Anson, C. E.; Powell, A. K. *Chem. Commun.* **2002**, 1054–1055. (b) Murugesu, M.; Clérac, R.; Pilawa, B.; Mandel, A.; Anson, C. E.; Powell, A. K. *Inorg. Chim. Acta* **2002**, *337*, 328–336 (c) Murugesu, M.; Clérac, R.; Anson, C. E.; Powell, A. K. *J. Phys. Chem. Solids* **2004**, *65*, 667–676. (d) King, P.; Clérac, R.; Anson, C. E.; Powell, A. K. *Dalton Trans.* **2004**, 852–861. (e) Murugesu, M.; King, P.; Clérac, R.; Anson, C. E.; Powell, A. K. *Chem. Commun.* **2004**, 740–741. (f) Murugesu, M.; Clérac, R.; Anson, C. E.; Powell, A. K. *Chem. Commun.* **2004**, 1598–1599.
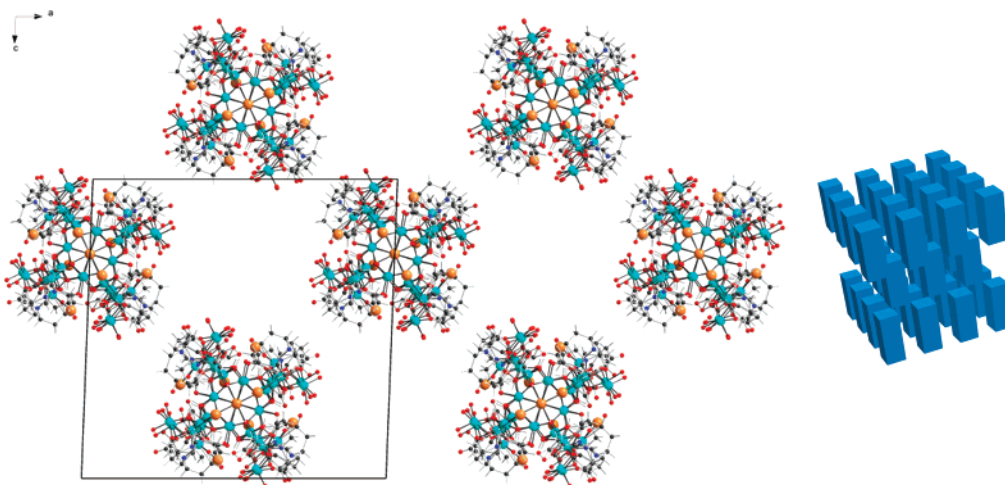
Figure 3. Packing diagram showing the arrangement of a layer of aggregates and cavities in the *ac*-plane and cartoon of the resulting 3D zeotypic structure.

Reaction of CuBr$_2$ (1 mmol) and the ligand H$_3$ntp, N(CH$_2$CH$_2$CO$_2$H)$_3$ (0.25 mmol), in water (15 mL) with a solution of CsOH·H$_2$O (1 mmol) in water (15 mL) results in the crystallization after 2 days of [Cu$_{44}$(μ_8-Br)$_2$(μ_3-OH)$_{36}$-(μ-OH)$_4$(ntp)$_{12}$Br$_8$(OH$_2$)$_{28}$]Br$_2$·81H$_2$O (**1**Br$_2$·81H$_2$O), in ~30% yield. The crystal structure[3] reveals not only that **1** is the largest Cu^{II} aggregate reported to date, but also that the packing arrangement of these leads to a very open super-structure. Figure 1 shows the complete structure of the Cu$_{44}$ molecule which can be more easily visualized in terms of its structural components. The overall shape of the inorganic core of the cluster approximates to a cuboidal framework of Cu^{II} centers held together by hydroxide bridges and anchored on to two bromide anions, which we believe act as templates for the structure, giving [Cu$_{24}$(μ_8-Br)$_2$(μ_3-OH)$_{24}$(μ-OH)$_8$]$^{14+}$ (Figure 2). This belief is based on our observation of the {KCl$_6$}$^{5-}$ scaffold in the Cu$_{36}$ compound and the fact that in that case other possible anionic templates led to different Cu^{II} compounds.[1b] This is also seems to be the case here, given that with other anions in this system we observe pseudo-Kagomé frameworks.[1c] The coordination spheres of these Cu^{II} centers are completed by carboxylate oxygens from eight [Cu(ntp)Br]$^{2-}$, four [Cu(ntp)(OH$_2$)]$^-$ moieties, eight [Cu(OH$_2$)$_3$]$^{2+}$ units, and eight OH$^-$ anions to give the whole Cu$_{44}$ aggregate **1**.

A crystallographic twofold axis lies through the two central μ_8-bromides, but the core structure itself corresponds to idealized D_{4h} symmetry. The aggregates form layers parallel to the *b*-axis (Figure 3), and since $a \approx c$ and $\beta \approx 90°$ this leads to a pseudotetragonal array. Each cuboidal aggregate is linked through its apices to eight further aggregates in the layers above and below via hydrogen bonding from a water ligand to a carboxylate oxygen. Consequently, the layers are organized such that each cavity in one layer is enclosed above and below by aggregates in the adjacent layers, resembling
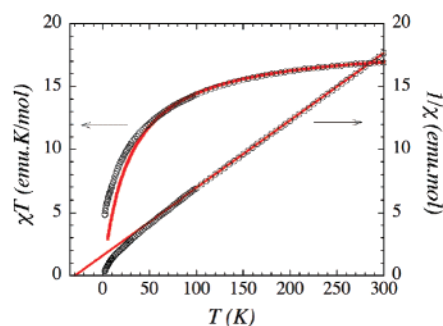
(2) Vilar, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1460−1477.
(3) **1**: C$_{108}$H$_{402}$Br$_{12}$Cu$_{44}$N$_{12}$O$_{211}$, *M* = 9161.10, monoclinic, *a* = 30.514(2) Å, *b* = 33.783(2) Å, *c* = 29.941(2) Å, β = 92.216(1)°, *V* = 30841(3) Å^3, *T* = 200(2) K, space group *C2/c*, *Z* = 4, *F*(000) = 18392, *D*$_c$ = 1.973 Mg m^{-3}, μ(Mo Kα) = 4.628 mm^{-1}; 75559 data, 34317 unique (*R*$_{int}$ = 0.1213), 1706 parameters, wR2 = 0.2217, *S* = 0.948 (all data), R1 = 0.0687 (14844 with *I* > 2σ(*I*)).

Figure 4. Temperature dependence of the χT product (where $\chi = M/H$ is the magnetic susceptibility) and $1/\chi$ for **1** at 1000 Oe. Solid line is the best fit obtained from a Curie−Weiss law.

tetragonally distorted body-centered cubic packing (Figure 3). The cavity dimensions are ~14 Å × 14 Å × 11 Å, contain the two bromide counterions and 81 waters of crystal-lization per aggregate, and are connected by channels running parallel to **a** + **c** (5.7 Å × 12.9 Å) and **a** − **c** (4.8 Å × 12.9 Å). The elemental analysis suggests that crystal water is lost very easily from the system with the values of C = 15.01, H= 3.94, and N = 1.90% equating to the loss of 29 water molecules from the formula unit (calculated values are C = 15.07, H = 3.98, and N = 1.95%). Structures with large solvent cavities and magnetic centers have been suggested for use in novel separation methods, and since this compound is composed of aggregates of paramagnetic metal centers, it was of interest to study its magnetic properties.

Solid state dc magnetic susceptibility measurements were collected on polycrystalline **1**Br$_2$·81H$_2$O from 300 to 1.8 K at 1000 Oe. The χT versus T and χ^{-1} versus T plots (Figure 4) show a Curie−Weiss behavior above ca. 60 K, with C = 18.6 emu·K·mol^{-1}, θ = −30 K. The Curie constant is consistent with 44 Cu^{II} centers, with *g* values of 2.12(2), and is in agreement with the broad EPR resonance line at *g* = 2.14(1) observed in a powder spectrum at room temper-ature. The negative Weiss constants indicate the presence of dominant antiferromagnetic interactions between spin carriers.

Below about 60 K, the magnetic measurements deviate significantly from the Curie−Weiss law suggesting that a
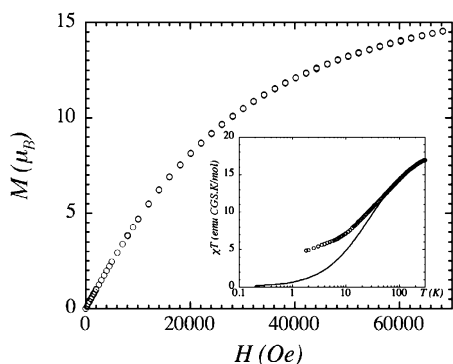
Figure 5. Field dependence of the magnetization for **1** at 1.83 K. Inset: χT versus T plot on a semilogarithm scale. Solid line is the best fit obtained from a Curie−Weiss law.

magnetic model considering the various internal magnetic pathways within the Cu_{44} aggregate should be analyzed to describe the low temperature data. However, an examination of the molecular structure suggests that 42 independent magnetic exchanges between Cu centers should be taken into account precluding the establishment of a model to find the ground spin state of the aggregate. Looking at the field dependence of the magnetization to try to gain some additional information on the magnetic properties shows that the problem is compounded by the presence of low lying magnetic states which are populated even at low temperature.

Thus, as shown in Figure 5, the magnetization rises smoothly to 14.6 μ_B at 7 T without saturation. This along with the fact that the χT versus T plot (inset of Figure 5) does not exhibit a clear plateau at low temperature supports the idea that the low lying excited states are still partially populated at 1.8 K. Furthermore, no fit to the field dependence of the magnetization could be obtained using Brillouin functions. However, since the χT product does not appear to extrapolate to zero at 0 K, it would seem that this Cu_{44} aggregate has a nonzero spin ground state. We plan to complement these preliminary magnetic measurements with lower temperature data in order to determine the spin ground state of this large and aesthetically pleasing Cu^{II} aggregate in parallel with a full thermogravimetric analysis.

Supporting Information Available: Crystallographic details (CIF) for **1**$Br_2 \cdot 81H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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