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

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Reaction of Cu(II) and the aminopolycarboxylate nitrilotripropionic acid ($H_3$ntp) in water leads to the formation of $[Cu_{44}(\mu_8\text{-}Br)_2(\mu_3\text{-}OH)_{36}(\mu\text{-}OH)_4(ntp)_{12}Br_8(OH_2)_{28}]Br_2{\cdot}81H_2O$. The $Cu_{44}$ aggregates have a central inorganic core corresponding to $[Cu_{24}(\mu_8\text{-}Br)_2(\mu_3\text{-}OH)_{24}(\mu\text{-}OH)_8]^{14+}$ 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 $\{M_xL_n(O)_y(OR)_z(HOR)_p\}^{\pm b}$ 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 even larger $Cu^{II}$ aggregate with 44 copper centers featuring two central bromide templates and a zeotypic superstructure.

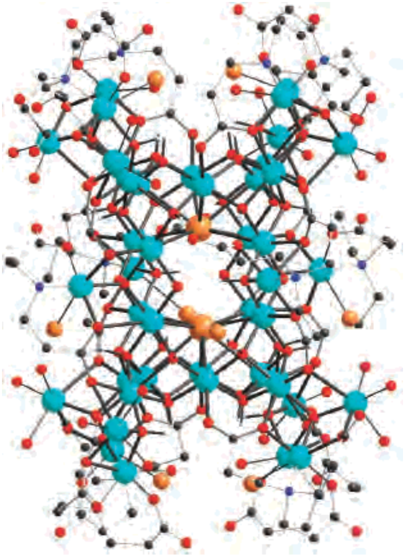

**Figure 1.** Structure of the $Cu_{44}$ aggregate **1**.

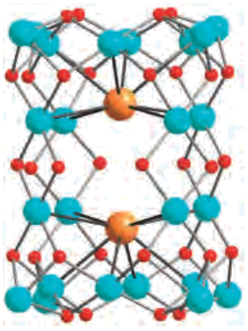

**Figure 2.** The inorganic $[Cu_{24}(\mu_8\text{-}Br)_2(\mu_3\text{-}OH)_{24}(\mu\text{-}OH)_8]^{14+}$ core in **1**.

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(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.

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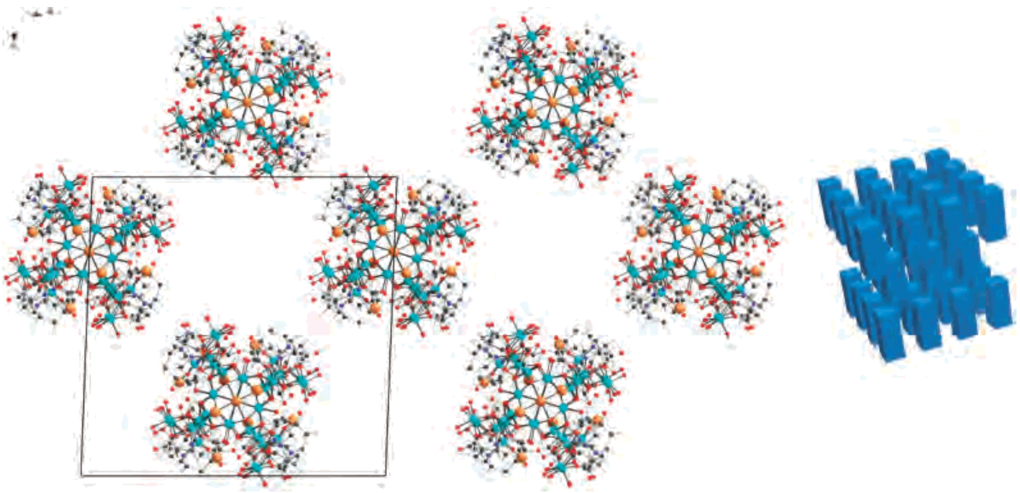

**Figure 3.** Packing diagram showing the arrangement of a layer of aggregates and cavities in the *ac*-plane and cartoon of the resulting 3D zeotypic structure.

Reaction of $CuBr_2$ (1 mmol) and the ligand $H_3ntp$, $N(CH_2CH_2CO_2H)_3$ (0.25 mmol), in water (15 mL) with a solution of $CsOH{\cdot}H_2O$ (1 mmol) in water (15 mL) results in the crystallization after 2 days of $[Cu_{44}(\mu_8\text{-}Br)_2(\mu_3\text{-}OH)_{36}(\mu\text{-}OH)_4(ntp)_{12}Br_8(OH_2)_{28}]Br_2{\cdot}81H_2O$ ($\mathbf{1}Br_2{\cdot}81H_2O$), 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 superstructure. 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 $[Cu_{24}(\mu_8\text{-}Br)_2(\mu_3\text{-}OH)_{24}(\mu\text{-}OH)_8]^{14+}$ (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**.

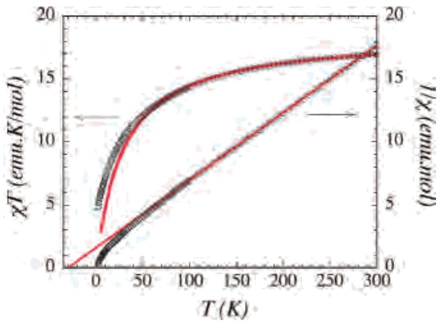

**Figure 4.** Temperature dependence of the $\chi T$ product (where $\chi = M/H$ is the magnetic susceptibility) and $1/\chi$ for **1** at 1000 Oe. Solid line is the best fit obtained from a Curie−Weiss law.

A crystallographic twofold axis lies through the two central $\mu_8$-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 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 crystallization per aggregate, and are connected by channels running parallel to $\mathbf{a} + \mathbf{c}$ (5.7 Å × 12.9 Å) and $\mathbf{a} - \mathbf{c}$ (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 $\mathbf{1}Br_2{\cdot}81H_2O$ from 300 to 1.8 K at 1000 Oe. The $\chi T$ versus $T$ and $\chi^{-1}$ versus $T$ plots (Figure 4) show a Curie−Weiss behavior above ca. 60 K, with $C = 18.6$ emu·K·mol$^{-1}$, $\theta = -30$ 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 temperature. 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

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(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, $\beta = 92.216(1)°$, $V = 30841(3)$ Å$^3$, $T = 200(2)$ K, space group $C2/c$, $Z = 4$, $F(000) = 18392$, $D_c = 1.973$ Mg m$^{-3}$, $\mu$(Mo K$\alpha$) = 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 $I > 2\sigma(I)$).

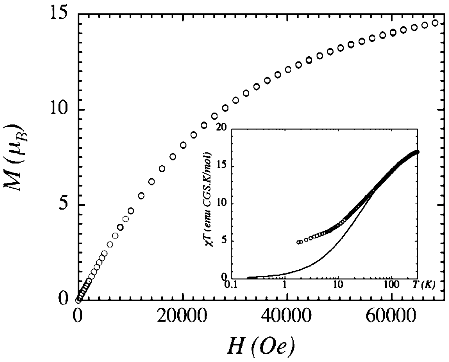

**Figure 5.** Field dependence of the magnetization for **1** at 1.83 K. Inset: $\chi T$ versus $T$ plot on a semilogarithm scale. Solid line is the best fit obtained from a Curie−Weiss law.

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 $\mu_B$ at 7 T without saturation. This along with the fact that the $\chi T$ 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 $\chi T$ 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.

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

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