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Structure and Magnetic Properties of a Hydroxo-Bridged Copper(II) Distorted Cubane Stabilized via Supramolecular Hydrogen Bonding with an Ionic Hexafluoroacetylacetonate

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Tetranuclear $[Cu^{II}_4(OH)_4(aib)_4)](hfac)_4$ (**1**; aib = 2-methyl-2-amino-4-iminopentane; hfac = hexafluoroacetylacetonate) forms from the reaction of aqueous ammonia and $Cu(hfac)_2\cdot2H_2O$ in acetone. The structure of **1** reveals that four noncoordinating $hfac^-$ counterions stabilize the distorted cubane complex via multiple H-bonding contacts. Magnetic susceptibility studies reveal that cubane-like **1** is best described as a pair of independent antiferromagnetically coupled dimers with $g = 2.10$ and $J/k_B = -298$ K (207 cm^{-1}) ($H = -2J\mathbf{S}_1\cdot\mathbf{S}_2$).

Transition-metal clusters having a cubane structure (M_4L_4) have attracted much attention because of their unusual physical properties and relevance to biological function in metalloproteins.[1,2] In particular, multinuclear complexes with superparamagnetic behavior that have a $[M_4(\mu_4\text{-}X_4)]$ core, where X = anion, are of considerable interest, and their structure−function relationship is the subject of intense investigation.[3] Paramagnetic metal clusters with bridging of hydroxo, alkoxo, azido, sulfido, or iminato ligands have been previously reported to show that small changes in structure

at the metal core can have far-reaching effects on the magnetic and optical properties. For example, the magnetic behavior at low temperature of Cu^{II}-containing cubane clusters can be ferromagnetic or antiferromagnetic depending on the first-coordination sphere, the Cu−Cu distances, and the steric and crystal packing forces. New examples of similar systems with well-described structural features and correlated physical properties are needed to further understand the magnetic exchange between the bridged metals. Herein, we report the facile synthesis, crystal structure, and magnetic properties of a hydroxo-bridged copper(II) cubane complex (**1**) that exhibits a unique set of supramolecular H-bonding contacts with four deprotonated hexafluoroacetylacetonate (hfac) anions, which influence the stability and bond distances between the paramagnetic centers. Because of the strong propensity to chelate, uncoordinated $hfac^-$ groups in the presence of transition metals are uncommon and have been observed in only a few compounds.[4]

The cubane complex $[Cu_4(aib)_4(OH)_4][(hfac)_4]$ (**1**) was isolated in 60% yield from a one-pot reaction that involves dissolution of $Cu(hfac)_2$ in a solution mixture of acetone and ammonium hydroxide (80:20).[5] During the reaction, the amino−imino ligand 2-methyl-2-amino-4-iminopentane (aib) was conceivably formed via metal-assisted Schiff-base and Aldol condensation of acetone with ammonia. Although such metal-assisted ligand formation has been observed for Pd^{II}, Co^{II}, and Ni^{II} ions,[6] this is the first report for a Cu^{II}-templated solvent condensation and the concurrent hfac displacement that results in the H-bonded stabilized cubane complex of **1** with $hfac^-$ anions. When the reaction is carried out in the

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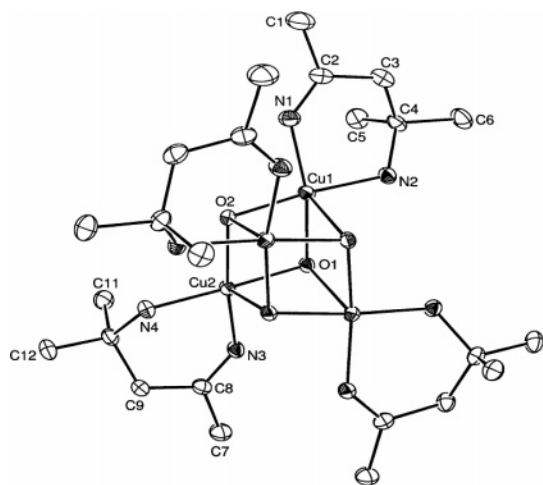
Figure 1. ORTEP (50% probability ellipsoids) atom-labeling structure of **1**. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Cu1−O2 1.946(2), Cu1−O2# 2.411(2), Cu1−O1 1.956(2), Cu2−O1# 2.411(2), Cu1−N1 1.957(3), Cu1−N2 1.980(3), Cu1−Cu2 3.0227(5), Cu2−O1 1.942(2), Cu2−O1# 2.424(2), Cu2−N3 1.952(3), Cu2−O2 1.962(2), Cu2−N4 1.977(4), O2−Cu1−O1 78.40(9), O1−Cu1−N2 96.72(11), N1−Cu1−N2 92.16(13), Cu2−O1−Cu1 101.70(10), Cu1−O2−Cu2 101.33(10).

absence of hfac⁻, e.g., when $Cu(O_3SCF_3)_2$ is used as the starting material, the reaction yields mononuclear $[Cu(aib)_2](O_3SCF_3)_2$.

Complex **1** is composed of two μ-hydroxocopper dimers assembled into a tetramer cubic structure (Figure 1). The coordination around each of the Cu^{II} centers is composed of one ligated aib group and three μ-hydroxide bridges and gives rise to a square-pyrimidal geometry around the metals. The equatorial sites of the Cu ions are occupied by the amino−imino moieties, and the O atoms from the hydroxide bridges are arranged around the metal in a *fac* configuration. Complex **1** has a crystallographic 2-fold axis, and the intracluster metal−metal separations of Cu2···Cu3 and Cu2···Cu4 are 3.14 and 3.36 Å, respectively, which are slightly longer than the other interatomic distances of the Cu centers (3.02 Å). The Cu1−O and Cu2−O intradimer distances range from 1.942(2) to 1.956(2) Å and average 1.952 Å; however, the interdimer distances are 2.411(2) and 2.424(2) Å and average 2.417 Å. As expected, the imine C2−N1 bond distance of 1.273(5) Å is shorter than the amine C4−N2 distance of 1.484(4) Å. The bridging angles of the Cu−O−Cu bonds, which determine the sign of the magnetic exchange interactions through O bridges, are in the range of
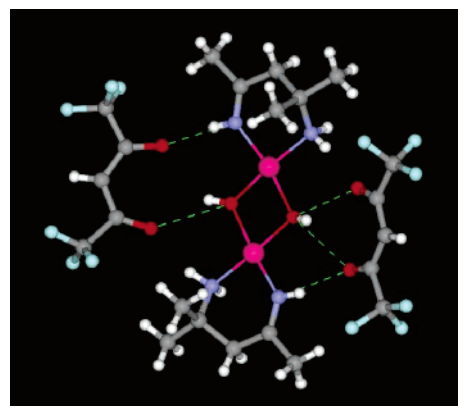
(5) Synthesis and selected data for **1**: To a solution of Cu(hfac)₂ (0.218 g, 0.44 mmol) in 12 mL of acetone was added 2 mL of a 25% ammonium hydroxide solution. The solution immediately changed from green to deep purple, indicating that the reaction was proceeding. After the addition of ammonium hydroxide, the solution was allowed to slowly evaporate for 2 days, giving deep-blue hexagonal prisms of **1** suitable for single-crystal X-ray diffraction. They were filtered on paper and air-dried for several hours. IR: ν(KBr)/cm⁻¹ 3525vs (O−H), 3259vs (N−H), 3237s (N−H), 3161w (N−H), 2978w (N−C), 1661s (C=O), 1600m (C−N), 1556s (C=O), from fingerprint 1526w, 1511w (C−C), 1249s, 1227s, 1196s, 1127s(C−C), 941w (OH) 789m (C−H), 657m (C−H). Elem anal. Calcd for $C_{22}H_{32}Cu_2F_{12}N_4O_6$: C, 32.88; H, 4.01; N, 6.97. Found: C, 33.25; H, 3.95; N, 6.97.
(6) (a) Alzuet, G.; Ferrer, S.; Cassanova, J.; Borras, J. *Inorg. Chim. Acta* **1993**, *205*, 79. (b) Fairlie, D. P.; Turner, M.; Byriel, K. A.; Mckeon, J. A.; Jackson, W. G. *Inorg. Chim. Acta* **1999**, *290*, 133.

Figure 2. H-bonding interactions by hfac⁻ anions and the asymmetric unit of **1**.

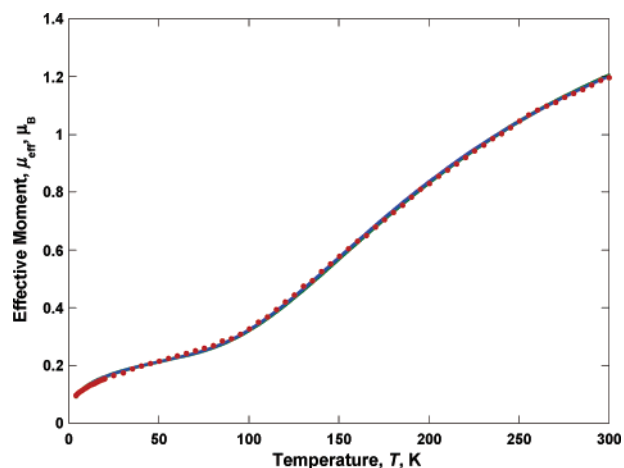**Figure 3.** $\mu_{eff}(T)$ for **1**, with the solid line being the fit with eq 1. $g = 2.10$, $J/k_B = -298$ K, $zJ'/k_B = 0$ K, $P_{imp} = 0.009$, $\theta_{imp} = -13$ K, and TIP $= 60 \times 10^{-6}$ emu mol⁻¹.

91.12(8)−101.70(10)°. The hfac⁻ counteranion interacts with the μ-hydroxo bridges via H-bonding interactions (Figure 2). These H-bonding interactions appear to be responsible for the solution and solid-state stabilization of **1** as well as the slight deviations in its structural parameters as compared to previously reported copper cubane systems.

Magnetic susceptibility measurements were made between 4 and 300 K.[7] At 300 K, the effective moment of **1**, μ_{eff} [$\equiv(8\chi T)^{1/2}$], was 1.19 μ_B per Cu. This was reduced from the spin-only value of 1.73 μ_B indicative of antiferromagnetic coupling between the bridging Cu^{II} ions. The magnetic moment decreased nearly linearly with decreasing temperature until ∼100 K, and below this temperature, it decreased less rapidly (Figure 3). Tetranuclear **1** is comprised of two dimers with a possible interaction between the two dimers as seen for other tetranuclear copper structures.[3b,8] Thus, the Bleaney−Bowers equation[9] ($H = -2J\mathbf{S}_1\cdot\mathbf{S}_2$), including a term for an $S = \frac{1}{2}$ paramagnetic impurity and a term to account for possible interactions between dimers, zJ', from the molecular field approximation, was used to fit the

(7) Using a Quantum Design MPMS-5 5T SQUID magnetometer at 1 T. All magnetic susceptibility measurements were made on polycrystalline samples contained in gel-cap holders at 1000 Oe with a Pd wire sample included in the sample to avoid problems of low signal. The data were corrected for the Pd wire standard and for diamagnetism calculated from Pascal's constants.

magnetic data (eq 1). The best-fit parameters were $g = 2.10$,[10] $J/k_B = -298$ K (207 cm^{-1}), $zJ'/k_B = 0$ K, $P_{imp} = 0.009$, $\theta_{imp} = -13$ K, and TIP $= 60 \times 10^{-6}$ emu mol^{-1}, indicating a strong antiferromagnetic coupling in the dimer and no coupling between dimers (Figure 3). The lack of coupling between the dimers that compose the cubane-like structure is ascribed to the 0.48 Å longer intradimer separation with respect to the interdimer separation, and, more importantly, it is because this superexchange pathway does not involve the $d_{x^2-y^2}$-like single-output, multiple-output orbital.

$$\chi_{dimer} = \frac{2Ng^2\mu_B^2}{T}\frac{1}{3 + e^{-2J/k_BT}}$$

$$\chi_{total/Cu} = \frac{1}{2}(1 - P_{imp})\frac{\chi_{dimer}}{1 - (2zJ'/Ng^2\mu_B^2)\chi_{dimer}} +$$
$$P_{imp}\frac{Ng^2\mu_B^2}{4k_B(T - \theta_{imp})} + TIP; \quad J \gg zJ' \quad (1)$$

Numerous studies of the magnetostructural correlation in dinuclear Cu^{II} complexes[11,12] led to the identification of two linear correlations: one between the coupling and the Cu$-$O$-$Cu angle and the other between the coupling and the Cu$-$Cu distance for μ-OH dinuclear copper compounds. The

observed Cu$-$O$-$Cu angle of 101.7(4)° correlates to strong antiferromagnetic coupling between Cu^{II} centers because this angle predicts $J = -215$ K from the linear correlation established by Hatfield and co-workers.[11] This is low compared to -298 K obtained from the fit to eq 1. The Cu$-$Cu distance of 3.023 Å correlates to strong antiferromagnetic coupling between Cu^{II} centers as observed and this distance predicts $J = -423$ K from the linear correlation established by Hatfield and co-workers. In this instance the correlation predicts a stronger antiferromagnetic coupling than the observed value of -298 K. This deviation from the previous correlations is attributed to the longer Cu$-$O bond length of 1.947 to 1.956 Å for **1** compared to the range of 1.895 to 1.93 Å used in the magnetostructural series. We also compared the result the relation between J and the Cu$-$O$-$Cu bridging angle for copper cubane structured materials.[3b] This relationship predicts $J/k_B = -355$ K for 101.7°, which, in contrast to the Hatfield relationship, exceeds the observed value.

In conclusion, the single multistep reaction yields a new copper cubane complex with outer-sphere H-bonding contacts that cause significant variations in the stability and solid-state bonding parameters of the metal cluster. Rational modifications of the in situ generated ligand or the hfac$^-$ anions may introduce structural changes at the metal core that could control magnetic anisotropy and control the magnetic interactions of the paramagnetic centers in similar cubane systems.

Supporting Information Available: Crystallographic data (atomic positions, thermal parameters, bond lengths, etc.) for **1** in the form of a CIF file. This material is available free of charge via the Internet at http://pubs.ac.org.

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