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Self-assembly of a High-Nuclearity Chloride-Centered Copper(II) Cluster. Structure and Magnetic Properties of [Au(PPh$_3$)$_2$][*trans*-Cu$_6$(μ-OH)$_6${μ-(3,5-CF$_3$)$_2$pz}$_6$Cl]

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A chloride-centered hexanuclear copper(II) pyrazolate [Au(PPh$_3$)$_2$]-[*trans*-Cu$_6$(μ-OH)$_6${μ-(3,5-CF$_3$)$_2$pz}$_6$Cl] is isolated from the reaction of the trinuclear copper(I) pyrazolate [Cu$_3${μ-(CF$_3$)$_2$pz}$_3$] with PPh$_3$AuCl and Ph$_3$P in moist air. The six copper atoms are bridged by pyrazolate and hydroxyl ligands, above and below the copper plane. The chloride anion exists at the center of the planar cavity formed by the copper atoms with Cu–Cl distances of 3.02–3.13 Å. The magnetic susceptibility measurements show a strong antiferromagnetic coupling between the copper centers with an estimated exchange constant of $J \approx 650$ cm^{-1}.

Anion-encapsulating assemblies mimic several biological processes.[1] Copper(II) pyrazolates form one-dimensional coordination polymers that change structure upon desorption of some small molecules.[2] The octanuclear copper complex [Cu$_8$(μ-OH)$_8$(μ-dmpz)$_8$] also shows catalytic activity for oxidation of organics.[3] The chemistry of the copper assemblies[4a,b] is reminiscent of work on the halide-centered studies of Gatteschi et al.[4c] and the chalcogenide-centered cubal copper(I) dialkyldithiophosphates.[5] Several metallacyclic copper(II) pyrazolates, [*cis*-Cu$_x$(μ-OH)$_x$(μ-pz)$_x$], where $x = 6$, 8, 9, 12, and 14, have been found in supramolecular assemblies that encapsulate anions through the OH bridges.[6] We report here the synthesis and structural characterization of a chloride-centered metallacyclic hexanuclear copper(II) pyrazolate anionic cluster where encapsulation also involves the copper(II) atoms.

The blue blocks prepared from the reaction of copper pyrazolate with PPh$_3$AuCl and Ph$_3$P in the presence of air are crystallized in the monoclinic space group $C2/c$.[7,8] Each copper atom is coordinated to two hydroxyl groups and two pyrazolate ligands in a square-planar arrangement. The structure of the title compound contains copper atoms in a cyclic arrangement with a Cu−Cu distance of ~3.07 Å (Figure 1).

The distance across the ring is 6.05−6.26 Å, which is smaller than it is in the [*cis*-Cu$_6$(μ-OH)$_6$(μ-pz)$_6$] complex, ~6.60 Å,[6] which binds halide through the OH bridges. This larger ring complex has Cu−O−Cu angles that range from 114.8(3) to 119.4(4)°. The chloride anion in the title compound sits at the approximate center of the cavity at distances of 3.02−3.13 Å from the copper(II) atoms, held in place by Coulombic attractions to the copper(II) ions and weak hydrogen bonding with the *trans*-hydroxyl groups at 2.77−3.61 Å.

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(7) Synthesis of [Au(PPh$_3$)$_2$][*trans*-Cu$_6$(μ-OH)$_6${μ-(3,5-CF$_3$)$_2$pz}$_6$Cl]: To a stirred, aerated CH$_3$CN solution (4 mL) containing 0.221 g of [μ(-3,5-CF$_3$)$_2$pzCu]$_3$ were added Ph$_3$PAuCl [0.0377 g (7.63×10^{-5} mol)] and Ph$_3$P (0.020 g). CH$_2$Cl$_2$ was added (0.5 mL) until the gold complex was completely dissolved. The colorless solution was stirred for 30 min and then left to evaporate in air. Slowly the solution became blue, and after few days, blue crystallographic quality crystals of the hexanuclear copper(II) cluster were isolated. Yield: 80%. Elem anal. Calcd for C$_{66}$H$_{42}$N$_{12}$ClF$_{36}$O$_6$P$_2$AuCu$_6$: C, 32.24; N, 6.84; H, 1.72. Found: C, 32.14; N, 6.83; H, 1.65. Electrospray ionization mass spectrometry (ESI-MS) shows an anion peak at m/z 1737 with a trinuclear pyrazolate + Cl peak at m/z 834.7.

(8) Crystal data for [Au(PPh$_3$)$_2$][*trans*-Cu$_6$(μ-OH)$_6${μ-(3,5-CF$_3$)$_2$pz}$_6$Cl]·CH$_3$CN: $M_w = 2540.88$, $a = 15.6725(11)$ Å, $b = 20.2095(11)$ Å, $c = 27.9054(17)$ Å, $\alpha = 90.00°$, $\beta = 94.6100(10)°$, $\gamma = 90.00°$, $C2/c$, $V = 8810.0(9)$ Å^3, $Z = 4$, R1 = 0.0524, wR2 = 0.1242.

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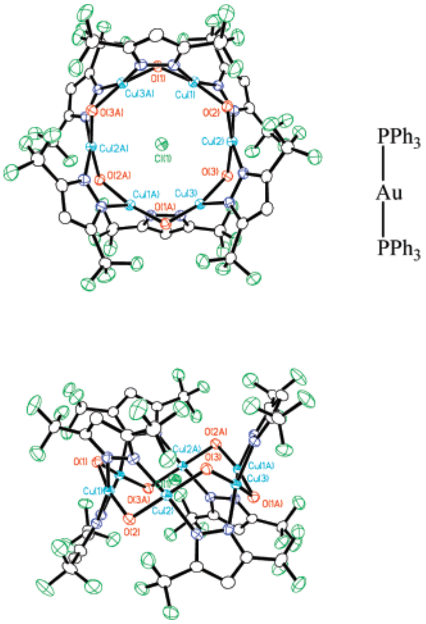

Figure 1. Top: Top view of $[\mathrm{Au(PPh_3)_2}][\mathit{trans}\text{-}\mathrm{Cu_6}(\mu\text{-OH})_6\{\mu\text{-(3,5-CF}_3)_2\text{-pz}\}_6\mathrm{Cl}]$ showing the chloride anion at the center of the cavity. Bottom: Side view showing the chloride anion at the same plane of the copper atoms. Selected bond distances (Å) and angles (deg): Cu(1)−O(2) 1.912(3), Cu(1)−O(1) 1.920(3), Cu(2)−O(3) 1.910(3), Cu(2)−O(2) 1.922(3), Cu(3)−O(3) 1.911(3), Cu(1)−N(2) 2.000(3); P(1)−Au(1)−P(1) 177.85(5), O(2)−Cu(1)−O(1) 168.71(12), O(3)−Cu(2)−O(2) 167.55(11), N(2)−Cu(1)−N(1) 163.05(13), N(4)−Cu(2)−N(3) 164.07(14), N(6)−Cu(3)−N(5) 163.94(13), Cu(1)−O(2)−Cu(2) 106.63(13), Cu(2)−O(3)−Cu(3) 106.64(12). Mean deviation of the Cu$_6$ plane, 0.0137 Å.

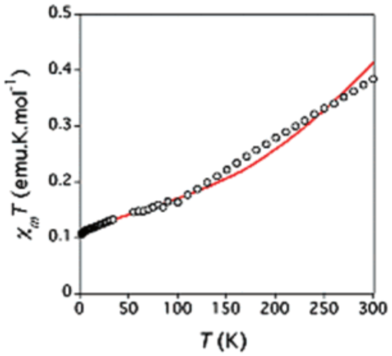

Figure 2. Temperature-dependent magnetic behavior for the title compound.

The dc magnetic susceptibility of **1** was studied in the 2−300 K range (Figure 2).[9] The $\chi_m T$ product at room temperature (0.38 emu·K·mol^{-1}) is small compared to the expected value for six magnetically isolated copper(II) centers (≈2.25 emu·K·mol^{-1}) and clearly indicates that the magnetic interactions between the copper(II) ions in the ring are antiferromagnetic. The $\chi_m T$ product decreases monotonically from room temperature down to 100 K (0.16 emu·K·mol^{-1}), where a change in the slope occurs, and $\chi_m T$ keeps decreasing at a slower pace and tends to 0.10 emu·K·mol^{-1} below 2 K.

The observed antiferromagnetic coupling is in good agreement with Cu−O−Cu angles over 106°. It has been well-established that the sign and magnitude of the magnetic exchange between the copper(II) centers through the oxo or hydroxo bridges are ferromagnetic for angles close to 90° but strongly antiferromagnetic for angles over 100°.[10] These results are similar to other ring compounds where the copper(II) ions are bridged by hydroxyl groups.[11]

Because the antiferromagnetic coupling in the hexanuclear ring yields a diamagnetic $S = 0$ ground state, the low-temperature regime must be dominated by a paramagnetic component, as is often observed in the magnetism of antiferromagnetic clusters. Indeed, the data in the 2−30 K range can be fitted to a Curie−Weiss law with the addition of a small temperature-independent paramagnetism, for $C = 0.112$ emu·K·mol^{-1}, $\theta = -0.12$ K, and $\chi_{\mathrm{TIP}} = 5.8 \times 10^{-4}$ emu·mol^{-1}. The magnetic behavior for six equivalent $S = {}^{1}/_{2}$ copper(II) ions, strongly coupled in a ring, can be represented by the isotropic Hamiltonian:

$$H = -2J[S_1S_2 + S_2S_3 + S_3S_4 + S_4S_5 + S_5S_6 + S_6S_1] \qquad (1)$$

The calculated magnetic susceptibility (χ_{ring}) for this Hamiltonian can be obtained by using the magnetism program *MAGPACK*.[12] Thus, the magnetic susceptibility can be modeled to $\chi T = \chi_{\mathrm{ring}}T + C/(T - \theta) + \chi_{\mathrm{TIP}}$. The best approximation obtained for an estimated $J \approx 650$ cm^{-1} ($g = 2.0$) is in very good agreement with the structural features of this compound.[10,11a] An entirely satisfactory fitting cannot be obtained, however. For the magnetic analysis, we have also neglected the intermolecular interactions, Cu···Cu = 7.9 Å, given the long distances between the hexanuclear copper rings in the lattice.

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Supporting Information Available: X-ray crystallographic file, in CIF format, for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) dc magnetic measurements were performed with an applied field of 2000 G in the 2−300 K temperature range with a Quantum Design SQUID magnetometer MPMS-XL. Data were corrected for the diamagnetic contributions calculated from the Pascal constants.

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