Formation and Stabilization of a Decanuclear Cu^{II} Wheel Linked by Chloride and O···H–N Hydrogen Bonds**

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Self-assembly by hydrogen bonding, π–π stacking, and van der Waals interactions are allvery important processes in the formation of biological architectures.[1] These mechanisms are being developed as efficient design tools in material sciences for organizing individual molecular motifs into highly ordered supramolecules.[2] Among these supramolecules, compounds with an unsupported cyclic structure are of particular interest, not only for their unique molecular shapes, but also for their potential as models of infinite one-dimensional chain complexes, and for studies of quantum-size effects.[3] Several of these unusual supramolecules are known;[4] however, major difficulties are how to control the growth of the metal chain along a pre-designated cyclic orientation and how small molecules can be included inside such wheels. Herein, we report a one-pot, high-yield synthesis of the largest known cyclic Cu^{II} cluster complex. The molecular assembly is generated and stabilized by two conventional inter-atomic attractive forces, namely, formation of Cl-Cu-Cl bonds and the ability of the oxygen atom of the amino alkoxide ligand $OC(CF_3)_2CH_2NHCH_2CH_2NMe_2$[5] to form a hydrogen bond to its central, secondary nitrogen atom.

Single-crystal X-ray structural analysis showed that complex **1** $[Cu^{II}ClL]_{10}$ ($L = OC(CF_3)_2CH_2NHCH_2CH_2NMe_2$) crystallizes in the triclinic space group $P\bar{1}$ with two $[Cu^{II}ClL]_{10}$ molecules in the unit cell.[6] One of these two similar molecules is shown in Figure 1. The structure consists of a large $Cu_{10}Cl_{10}$ cyclic framework, with its center on a crystallographic center of inversion. Taken individually, each Cu^{II} center in **1** is coordinated in a distorted square-pyramidal geometry with two nitrogen atoms, one oxygen atom, and one chlorine atom occupying the basal positions, and with a second chlorine atom from the neighboring $[Cu^{II}ClL]$ fragment occupying the axial position and acting as a bridge between two Cu^{II} centers. The Cu–O bonds span the range 1.934–1.944(3) Å, while the Cu–N bonds to the nitrogen atoms (N2, N4, N6, N8, and N10) (1.999–2.024(4) Å) are much shorter than those to the terminal NMe_2 groups (N1, N3, N5, N7, and N9; 2.071–2.089(4) Å). Moreover, the Cu–Cl(basal) bonds (2.248–2.267 Å) are much shorter than the Cu–Cl(axial) bonds (2.573–2.738 Å), but still well within the range expected for significant Cu–Cl coordination.[7]

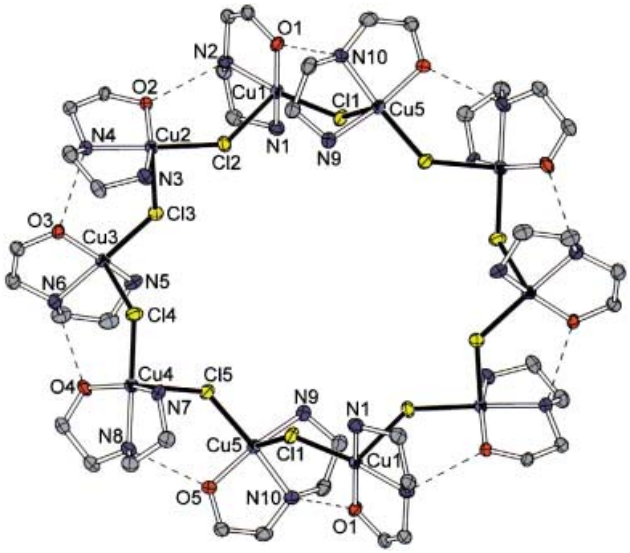

Figure 1. ORTEP drawing of complex **1** (thermal ellipsoids set at the 50% probability); all the CF_3 and Me groups have been omitted for clarity. Selected bond lengths [Å]: Cu1-O1 1.942(3), Cu1-N1 2.078(4), Cu1-N2 1.999(4), Cu1-Cl1 2.267(1), Cu1-Cl2 2.653(1), Cu2-Cl2 2.266(1), Cu2-Cl3 2.573(1), O2···N2 2.834(1).

The oxygen atom of each fluoroalkoxide terminus is located very close to the central N–H group of the neighboring $[Cu^{II}ClL]$ unit (c.f. O2···N2 = 2.834(1) Å and O1···N10 = 2.905(2) Å). These contacts are within the range of values found for medium-strong N–H···O hydrogen bonds observed in metal complexes (O···N = 2.69–2.98 Å).[8] It appears that this N–H···O hydrogen bonding is the intramolecular force that is responsible for holding the amino alkoxide ligand in a perpendicular configuration and simultaneously stabilizing the $Cu_{10}Cl_{10}$ ring structure.

Furthermore, all the CF_3 functional groups reside around the outer periphery, while the methyl substituents of the NMe_2 functional groups point towards the interior of the ring. The ring diameter, defined as the distance between two symmetry related, opposing copper atoms, ranges from 11.98(8) to 13.94(9) Å for the atoms Cu5 and Cu3, respectively. This packing arrangement creates a rectangular hole 3.5 × 6 Å, sufficient to incorporate small molecules such as organic solvents. In fact, and most surprisingly of the two Cu^{II}

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wheels within the asymmetric unit, one is found to be empty, while the second contains two acetonitrile solvent molecules.

To our knowledge, the molecular arrangement of complex **1** is unique. Only two other, smaller, cyclic molecules with Cu^{II} centers have been reported: one is the "flywheel" complex which contains six inner Cu^{II} metal centers,[9] while the other is an octameric Cu^{II}–pyrazolate complex[10] which possesses a copper-containing, cyclic or metallacrown skeletal arrangement.[11] The wheel structure composed of other transition metal elements has been observed in the Mn^{III} and Fe^{III} salicylhydrazidate complexes,[12] and for Fe^{III} alkoxide and Cr^{III} acetate complexes.[13]

Figure 2 shows the molar effective magnetic moment (μ_{eff}) as a function of temperature. In the temperature range 300–40 K, the μ_{eff} remains nearly constant. At 300 K, the μ_{eff} has a value of 5.76 μ_B, which corresponds to a combination of ten

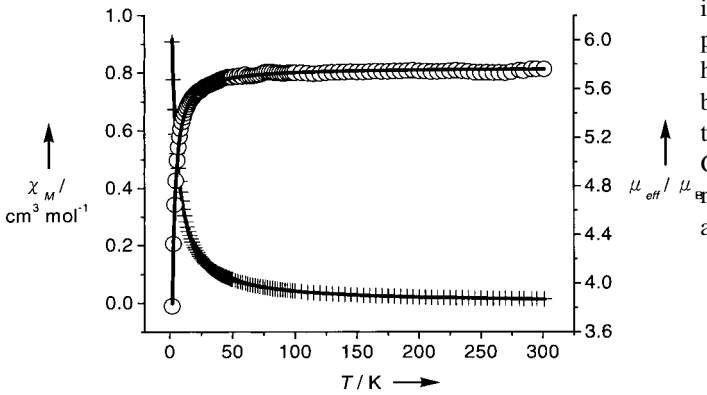

Figure 2. The magnetic susceptibility and effective magnetic moment of **1** are plotted as a function of temperature. The data were obtained from a powder sample of **1** at an external field of 1 Tesla. The solid lines in the magnetic susceptibility are the best-fitting calculated curves to Equation (2).

weakly interacting Cu^{II} centers ($S = 1/2$, 1.83 μ_B per Cu^{II}, $g =$ 2.112 obtained from ESR measurement of a powder sample at 298 K). Upon cooling below 40 K, the μ_{eff} decreases very quickly, and reaches a value of 3.81 μ_B at 2 K. The decrease in the μ_{eff} at low temperatures is a characteristic of antiferromagnetically coupled metal centers. To deduce the exchange parameter J, the experimental molar magnetic susceptibility χ_M versus temperature T (see Figure 2) was analyzed according to the modified Heisenberg alternating linear-chain model. The spin Hamiltonian, for such a chain is given in Equation (1) where $n = 10$ for ten Cu^{II} nuclei, $\boldsymbol{S}_{11} \equiv \boldsymbol{S}_1$, and $0.4 < \alpha \leq 1.0$.[14]

$$\mathcal{H} = -2J\sum_{i=1}^{n/2}(\boldsymbol{S}_{2i}\boldsymbol{S}_{2i-1} + \alpha\boldsymbol{S}_{2i}\boldsymbol{S}_{2i+1}) \quad (1)$$

The susceptibility[14] used to fit the data is given in Equation (2) where $\chi_M =$ molar magnetic susceptibility, $x = |J|/kT$, $N =$ Avogadro number, $\beta =$ Bohr magneton, $k =$ Boltzmann constant, and $T =$ temperature.

$$\chi_M = 10\frac{Ng^2\beta^2}{kT}\frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3} \quad (2)$$

The parameters used in fitting the least-squares curve are: $A = 0.25$, $B = -0.13695 + 0.26387\alpha$, $C = 0.017025 - 0.12668\alpha + 0.49113\alpha^2 - 1.1977\alpha^3 + 0.87257\alpha^4$, $D = 0.070509 + 1.3042\alpha$, $E = -0.0035767 - 0.40837\alpha + 3.4862\alpha^2$-$0.73888\alpha^3$, and $F = 0.36184 - 0.065528\alpha + 6.65875\alpha^2 - 20.945\alpha^3 + 13.585834\alpha^4$. The best least-squares fitting results in a small negative J value of -1.19 cm^{-1} and $\alpha = 0.9$, which indicates a very weak intramolecular antiferromagnetic coupling between the adjacent Cu^{II} centers. The small negative J value must arise because the unpaired electron on each Cu^{II} center is almost orthogonal to its neighbors. This situation occurs because the chloride bridge is asymmetric, with the long Cu–Cl bond not involved in a magnetic orbital. In the magnetization (M) versus external magnetic field (H_0) experiment recorded at 5 K, the magnetization increases monotonically as H_0 increases. At $H_0 = 5$ Tesla, the magnetization still does not saturate, which is typical behavior of noncoupled systems.

The corresponding bromide analogue [$Cu^{II}BrL$] (**2**) was isolated in 97% yield and a single-crystal X-ray analysis performed.[15] The solid-state structure of **2** consists of a hexanuclear complex, composed of two structurally similar, but crystallographic independent [$Cu^{II}BrL$]$_3$ fragments within the unit cell (Figure 3). In both trinuclear entities, all the Cu–N and Cu–O bonds are regular and their lengths are nearly identical to those of **1**. However, only two Cu^{II} atoms adopt the expected square-pyramidal geometry, while the

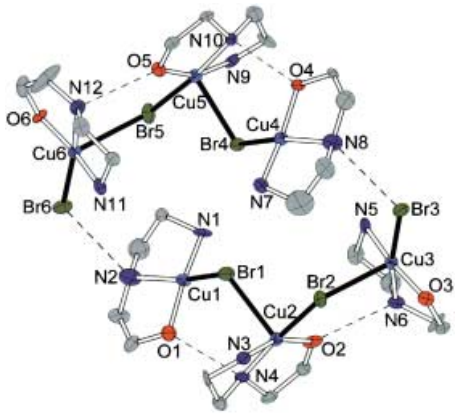

Figure 3. ORTEP drawing of complex **2** (thermal ellipsoids set at 50% probability); all the CF_3 and Me groups have been omitted for clarity. Selected bond lengths [Å]: Cu1-N1 2.02(1), Cu1-N2 2.05(1), Cu1-O1 1.899(9), Cu1-Br1 2.352(2), Cu2-Br1 2.827(2), Cu2-Br2 2.412(2), Cu3-Br2 2.812(2), Cu3-Br3 2.424(2), O1···N4 3.04(2), O2···N6 3.11(1), Cu1···Br6 4.711(2), Cu4···Br3 4.653(2), N2···Br6 3.50(1), N8···Br3 3.43(1).

third has a distorted square-planar arrangement with dihedral angles between the CuN_2 and CuOBr planes of 30.3° at the Cu1 and 27.8° at the Cu4 centers. This tetrahedral distortion results from a lack of Br→Cu apical interactions and the occurrence of Br···H–N hydrogen bonding (Br···N = av 3.47 Å). Such an interaction has also been seen in the cage supramolecule [$Ni_6(atu)_8Br]Br_3$ (Br···N = 3.33–3.40 Å; Hatu = amidinothiourea)[16] where the H bond terminates the growth of the metal chain. In our compounds the average Cu–Br bond is about 0.1 Å longer than the respective Cu–Cl bond in complex **1**, and therefore the lengthening of the Cu-Br-Cu distance also increases the O···N separation between

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the adjacent amino alcoholate ligands to 2.95–3.10 Å, which clearly results in weaker interligand hydrogen bonding. It seems that both the tetrahedral distortion and a reduction in the strength of N–H···O bonding are major factors that destabilize the decanuclear configuration, and forms the bis-trinuclear structure.

Both complexes **1** and **2** are highly soluble in polar solvents such as acetone, methanol, and acetonitrile, less soluble in THF, and insoluble in less polar media such as diethyl ether and chlorinated hydrocarbons. Thus, smaller aggregates from the Cu^{II} complex **1** are likely to be present in polar solvent, since polar solvents might disrupt the hydrogen bonding and chloride–metal dative bonding; otherwise, these complexes should exhibit limited solubility if the solid-state structures remain intact. In fact, electrospray mass spectrometry data of **1** in acetonitrile gave a series of fragmentation ions with formula $\{[Cu^{II}ClL]_n-Cl\}$ ($n=2-8$) within the detection limit of the instrument, m/z: 3000. Similar spectral patterns were also obtained with the bromide complex **2**. These observations are consistent with the proposed disintegration of the metal wheel structure in polar solvents.

In summary, these results indicate that the asymmetric amino alkoxide ligand allows the assembly of wheel-shaped supramolecules by utilization of strong interligand O···H–N hydrogen bonds. Variations in the ligand may lead to different wheel sizes and, therefore, to the inclusion of different small molecules. Ongoing studies deal with crystallizations in various solvents and with small molecules. The structural diversity of the supramolecules $[Cu^{II}XL]_n$, X = Cl and Br, is further exemplified by the crystal structure of complexes **1** and **2**. Changing the coordinated anion from chloride to bromide ion can significantly alter the molecular structure and the magnetic properties by increasing the interatomic Cu···Cu distance and decreasing the length and strength of hydrogen bonding. The larger negative exchange parameter in **2** ($J=-3.40\ cm^{-1}$), than **1**, is attributed to the stronger magnetic coupling resulting from the nonorthogonal intersection between the adjacent $[Cu^{II}BrL]$ units.

Experimental Section

Synthesis of the Cu^{II} complexes: The sodium alkoxide of approximate formula [NaL], $L=OC(CF_3)_2CH_2NHCH_2CH_2NMe_2$, was prepared by deprotonation of the amino alcohol LH (4.0 g, 14.9 mmol) with excess sodium hydride (0.43 g, 17.9 mmol) in THF solution at 0 °C. The solution was filtered to remove the sodium hydride. The filtrate was treated with 1.2 equivalents of $CuCl_2$ (2.4 g, 17.9 mmol) at room temperature. After 12 hours, the solution was filtered to remove the insoluble NaCl and the filtrate concentrated to dryness. The residual was purified by recrystallization from a mixture of acetonitrile and diethyl ether, to give the cyclic compound $[Cu^{II}ClL]_{10}$ (**1**, 3.05 g, 0.83 mmol) as a royal blue crystalline solid in 56% yield. The bromide complex **2** was obtained similarly in 97% yield.

The magnetic susceptibility of powder samples was measured in a SQUID magnetometer (Quantum Design, model: HPHS-5) at an external magnetic field of 1 Tesla in the temperature range of 300–2 K. All data were corrected for diamagnetism by using Pascal's constants for all the constituent atoms. Magnetic moments were calculated according to the equation $\mu_{eff}=2.828\sqrt{\chi_M T}$. In the least-squares fitting the residue function R is defined as $R=\Sigma(\chi_{M\,obs}-\chi_{M\,calcd})^2/\Sigma(\chi_{M\,obs})^2$. The least-squares residue value R is 6.39×10^{-5} for the complex **1**, and 1.05×10^{-3} for the complex **2**.

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[6] Crystal data for **1**: $C_{84}H_{129}Cl_{10}Cu_{10}F_{60}N_{22}O_{11.5}$, $M_r=3760.99$, triclinic, space group $P\bar{1}$, $a=15.3193(9)$, $b=17.899(1)$, $c=29.874(1)$ Å, $\alpha=103.239(1)$, $\beta=101.807(1)$, $\gamma=100.634(1)^\circ$, $V=7571.6(7)$ Å^3, $T=150$ K, $Z=2$, $\mu(Mo_{K\alpha})=1.678\ mm^{-1}$, 70160 reflections collected, 30945 unique ($R_{int}=0.035$), final wR_2(all data) = 0.1555. $R_1[I>2\sigma(I)]=0.0468$. Two acetonitrile molecules and 1.5 water molecules were also located in the unit cell. ESI MS (^{63}Cu): highest m/z 2894, $[Cu^{II}ClL]_8-Cl$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-172596 (**1**), and 172597 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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