# Synthesis, Structure, and Ferromagnetic Behavior of Decacopper(II) Cluster Complex Supported by Hexaanionic *p-tert*-Butylthiacalix[6]arene

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Synthetic strategies to produce nanosized metal complexes often employ large macrocyclic ligands with the ability to coordinate to several metal ions.[1] L. K. Thompson and co-workers reported octa- and dodecacopper(II) complexes[1a] which consist of μ_3-oxo-bridged subunits each containing a tetra- or hexanucleating macrocyclic ligand. Calixarenes with heteroatoms on the rims and in the body are excellent candidates as ligands for making multinuclear metal complexes.[2−6] Recently, we reported several complexes having *p-tert*-butylthia-,[3] *p-tert*-butylsulfinyl-,[5] and *p-tert*-butylsulfonylcalix-[4]arenes[6] (X = S, SO, and SO_2, respectively; *n* = 4) as multidentate ligands coordinated to first- and second-row transition metal ion-(s).
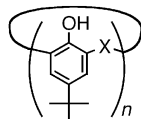
Under appropriate conditions, the calix[4]arene derivatives can act as a building unit to form multinuclear complexes.[5] A larger calixarene such as *p-tert*-butylthiacalix[6]arene (X = S; *n* = 6; $H_6\mathbf{L}$)[7] can act as a large macrocyclic ligand to which several metal ions can be bound via oxygen and sulfur atoms to form a phenoxy-bridged cluster-core. Thus, $H_{6-n}\mathbf{L}^{n-}$ can be used as a building unit to produce metal-containing nanostructures. In this communication, we describe a novel decacopper(II) cluster complex supported by two $\mathbf{L}^{6-}$ and other supporting ligands (O^{2-}, OH^-, and AcO^-).

Reaction of $Cu(AcO)_2$ and $H_6\mathbf{L}$ in $CH_2Cl_2/MeCN$, followed by recrystallization from $CHCl_3/dmf$, gave deep red crystals of $[Cu_{10}\text{-}(\mathbf{L})_2(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_3(\mu\text{-}AcO)]\cdot8dmf\cdot6H_2O$. Figure 1 shows the structure of the complex.[8,9] The complex has a crystallographic two-fold axis which divides the complex into two pentacopper(II) units. In the complex, $\mathbf{L}^{6-}$ takes a "pinched-cone" conformation (Chart 1) having a pocketlike structure where four phenoxy oxygens (O1, O3, O4, and O6) are in a square-planar arrangement.

Figure 2 shows the structure of the decacopper(II) core. Cu1 is located in the center of the oxygen square with bond lengths between 1.941(2)−2.0154(19) Å. Five copper(II) ions (Figure 2, drawn with filled bonds) are included in the pocket, forming a square pyramid. The four basal coppers (Cu2−Cu5) are placed above the phenoxy oxygens with standard Cu−O distances of 1.9660(19) and 2.0125(18) Å for Cu2 and Cu5 and with longer distances of 2.208(2) and 2.276(2) Å for Cu3 and Cu4, respectively.
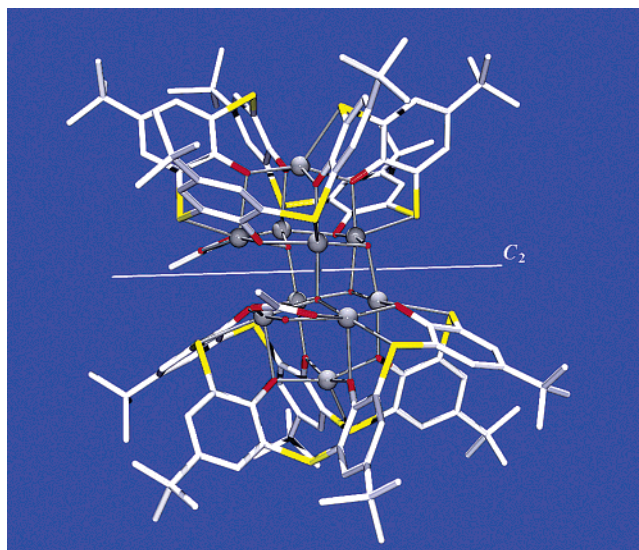

Figure 1. Crystal structure of the decacopper(II) complex.
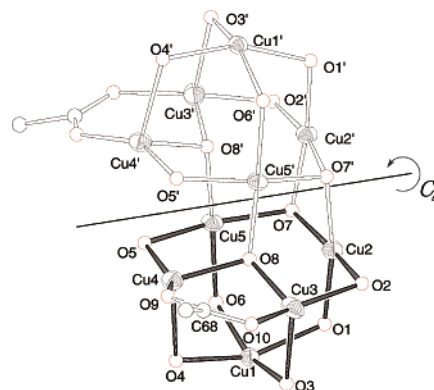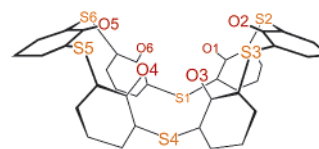

Figure 2. Decacopper(II) core structure with thermal ellipsoids at 40% probability for Cu atoms. Primed atoms were generated using the symmetry transformation −x + 1, y, −z + 1/2.

Chart 1

O2 and O5 connect two pairs of copper(II) ions (Cu2/Cu3 and Cu4/Cu5, respectively) in the basal plane with bond lengths of 1.942-(2)−2.001(2) Å. The four basal coppers are further connected by

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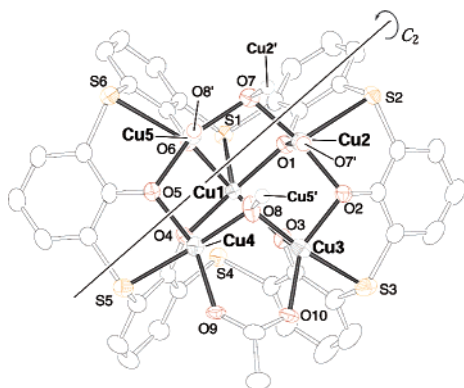‡ Graduate School of Engineering, Tohoku University.

Figure 3. ORTEP diagram of one pentacopper(II) unit with thermal ellipsoids at 40% probability. *tert*-Butyl groups and hydrogen atoms are omitted.
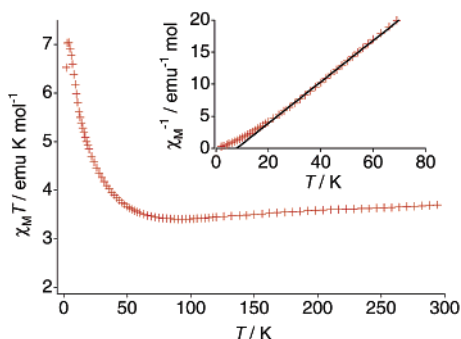

Figure 4. Temperature dependence of $\chi_M T$ and χ_M^{-1} (inset) for the decacopper(II) complex. The solid line corresponds to the best fit based on the Curie−Weiss expression.

hydroxo (O7), oxo (O8), and acetate groups(O9 and O10).[8] Around the crystallographic two-fold axis, the two pentacopper(II) units are connected via O7 and O8 to form decacopper(II) core. Each copper(II) atom is further coordinated by a sulfur atom from $\mathbf{L}^{6-}$ (Figure 3), and all copper atoms are regarded as being in a distorted square-pyramidal environment with the basal planes including O_4 donor sets for Cu1, Cu2, and Cu5 (Figure 2), and O_3S donor sets for Cu3 and Cu4.

The ESI mass spectrum of an acidic EtOH solution of the complex shows a clear signal corresponding to [Cu₁₀(**L**)₂(O)(OH)₄-(AcO)(H₂O)]⁺ ($m/z = 2946.79$) showing that the decacopper(II) core structure remains intact in solution.

The magnetic behavior of the decacopper(II) core is shown in Figure 4 as a $\chi_M T$ versus T plot.

The $\chi_M T$ value at 300 K, 3.73 emu K mol⁻¹, is compatible with the spin only value for the dilute 10 magnetic centers ($S = \frac{1}{2}$) with a g value of 2.00, which is nearly constant down to 50 K. Below 50 K, $\chi_M T$ increases rapidly to reach a maximum value of 7.04 emu K mol⁻¹ at 4 K, suggesting a ferromagnetically coupled behavior in the core. The magnitude of the interaction was estimated as $\theta = 7.9(2)$ K on the basis of the Curie−Weiss model (Figure 4, inset). Simulation of the temperature dependence of $\chi_M T$ was not performed due to the complexity of the structure. However, some ferromagnetic pathways can be found in the decacopper(II) core. As mentioned above, all copper(II) ions are in a distorted square-

pyramidal coordination environment, and each magnetic orbital ($d_{x^2-y^2}$) lies in the basal plane. The dihedral angles between basal planes for Cu1/Cu2, Cu1/Cu5, Cu2/Cu3, Cu2/Cu5, and Cu4/Cu5 are estimated as 85.78(9)°, 85.65(9)°, 80.28(12)°, 89.09(7)°, and 77.08(12)°, respectively. Furthermore, Cu2 and Cu2′ are connected by di-μ-hydroxo bridges with a bridging angle of 96.84(12)°. All these structural features are advantageous for orthogonality between adjoining magnetic orbitals.[10] Although there are some possible antiferromagnetic pathways in the core, overall magnetic behavior of the complex turns out to be ferromagnetic.

In this study, we have successfully used thiacalix[6]arene to produce a ferromagnetically coupled copper(II) decamer. Because this macrocyclic ligand has a large number of donor atoms that can bind up to five metal atoms in the pinched-cone conformation, it is an excellent tool for making nanocomplexes.

Supporting Information Available: Experimental procedure for the preparation of the complex, ESI MS, and details of X-ray crystallographic analysis (PDF). X-ray crystallographic file (CIF). This material is avilable free of charge via the Internet at http://pubs.acs.org.

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(8) Crystal data: [Cu₁₀(**L**)₂(μ₃-O)₂(μ₃-OH)₃(μ-AcO)]·8dmf·6H₂O, C₁₄₆H₂₀₆-Cu₁₀N₈O₃₃S₁₂, $M = 3605.35$, $T = 200(2)$ K, monoclinic, $C2/c$, $a = 30.043$-(3) Å, $b = 17.1273(18)$ Å, $c = 35.197(4)$ Å, $\beta = 97.659(2)°$, $V = 17950(3)$ Å³, $Z = 4$. R1 = 0.0573, wR2 = 0.1635 ($I > 2\sigma(I)$) for 20437 independent reflections. Final atomic coordinates, displacement parameters, and full bond lengths of the structures are given as the Supporting Information.

(9) Both μ-OH⁻ (O11) and μ-AcO⁻ are found between Cu3 and Cu4 as bridging ligands by the differential Fourier calculation. They were refined each with 50% occupancy giving appropriate thermal displacement parameters for both ligands. Hence, Cu3 and Cu4 are bridged by μ-OH⁻ or μ-AcO⁻ with the same probability. Only the acetate group(s) are shown in Figures 1−3.

(10) For example: Kahn, O. *Molecular Magnetism*; VCH: New York, 1993 and references therein.

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