

A *p*-*tert*-Butyldithiacalix[4]arene-Copper(II) Complex Having Double-cone Shape of Unique Heteroditopic Inclusion Behavior

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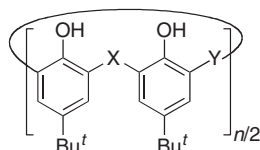
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X-ray diffraction revealed a single crystal of a Cu(II) complex of *p*-*tert*-butyldithiacalix[4]arene **5** (H_4L) to be $[Cu_3(HL)(H_2L)(AcO)]$, in which three Cu(II) ions are sandwiched by two calixarene ligands including different guest molecules, $CHCl_3$ and hexane, in each cone-shaped cavity.

Multinuclear metal complexes have been extensively investigated from the interests in their structural complexity and diversity, and physicochemical properties arising from cooperative effects by multimetal ions.¹ Recently, we have elucidated that tetrathiacalix[4]arene (**1**)² as well as the analogues such as hexathiacalix[6]arene^{3,4} (**2**), tetrasulfinyl- (**3**),⁵ and tetrasulfonylcalix[4]arene (**4**)⁶ are a suitable ligand for the formation of multinuclear complexes, because of the multidentate fashions provided not only by phenoxo oxygen but also by the bridging groups (S, SO, and SO_2 at X and Y).



	X	Y	n
1	S	S	4
2	S	S	6
3	SO	SO	4
4	SO_2	SO_2	4
5	S	CH_2	4

Very recently, we reported a convenient synthesis of *p*-*tert*-butyldithiacalix[4]arene **5** in which phenol units are linked by sulfide and methylene alternately,⁷ allowing us a solvent extraction study to reveal that **5** selectively binds to Cu(II) ion among various transition-metal ions. This was rather unexpected because tetrathia counterpart **1** shows strong affinity to a wide range of so called "soft" to intermediate metal ions including Cu(II) owing to the O,S,O-tridentate coordination manner.⁸ Since **5** has two sets of O,S,O donors, isolated by two methylene linkages, it seemed of interest to contrast the difference between the structures of Cu(II) complex of **1**⁹ and **5**, and herein we report the synthesis of a Cu(II) complex of **5** having three metal centers with two cone-shaped ligands of unique heteroditopic inclusion behavior.

The Cu(II) complex of **5** was prepared by stirring a mixture of **5**⁷ and sevenfold excess of $Cu(AcO)_2$ in $CHCl_3/CH_3CN$ (1/1, v/v) at ambient temperature for 8 h. After removing solvent, the residue was washed with a small amount of water. Slow diffusion of hexane into $CHCl_3$ solution of the complex gave deep red single crystals in 64% yield.

The crystal structure of the complex is shown in Figure 1.¹⁰ The Cu(II) complex of **5** (H_4L) was revealed to have composition of $[Cu_3(HL)(H_2L)(AcO)]$, in which calix ligands HL^{3-} and H_2L^{2-} in cone conformation are fused at the lower rims by coordinating to three Cu(II) ions to show typical double-cone structure. The trianionic HL^{3-} and dianionic H_2L^{2-} serve as octa- and hepta-dentate ligands, respectively (see also Figure 2),

whereas one acetate acts as a monodentate ligand for Cu1. There are two kinds of coordination geometry around Cu(II) ions. The Cu2 is in a square-pyramidal O_4S coordination geometry consisting of an apical O5 and an O_3S -basal plane of phenolic O1,

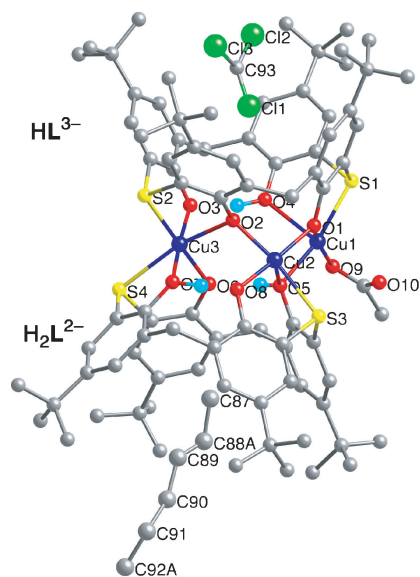


Figure 1. Crystal structure of $[Cu_3(HL)(H_2L)(AcO) \cdot C_6H_{12} \cdot CHCl_3]$. The hydrogen atoms except phenol OH are omitted for clarity. The included $CHCl_3$ and hexane molecules are disordered and one of the positions are drawn. Selected atomic distances (Å): Cu1–O1 1.921(2), Cu1–O4 2.397(2), Cu1–O5 2.022(2), Cu1–O9 1.927(2), Cu1–S1 2.3457(10), Cu2–O1 1.938(2), Cu2–O2 1.941(2), Cu2–O5 2.268(2), Cu2–O8 1.910(2), Cu2–S3 2.4203(10), Cu3–O2 2.3549(18), Cu3–O3 1.910(2), Cu3–O6 2.038(2), Cu3–O7 1.984(2), Cu3–S2 2.3172(11), Cu3–S4 2.6620(9), Cu1–Cu2 3.105, Cu1–Cu3 4.742, Cu2–Cu3 3.565.

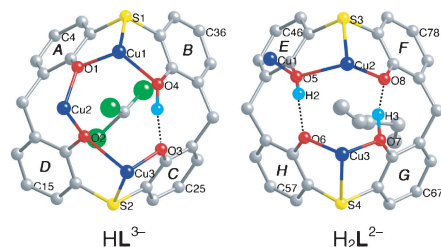


Figure 2. Top views of the structures of HL^{3-} and H_2L^{2-} . For clarity, *tert*-butyl groups and hydrogen atoms except those of hydroxy are omitted. Hydrogen bondings are drawn as broken lines. Torsion angles of distal aromatic planes ($^\circ$): A–C 46.0, B–D 82.9, E–G 61.7, F–H 62.6.

O2, O8, and sulfide S3. Similar O₄S coordination geometry is provided to Cu1 with the aid of acetate O9.

By contrast, Cu3 is in a distorted octahedral environment consisting of equatorial O₃S and axial OS (O2, S4) donor sets from the calixarenes. As can be seen, phenoxo O1 and phenol O5 bridge Cu1 and Cu2 centers, whereas phenoxo O2 bridges Cu2 and Cu3 centers to form multinuclear coordination core.

Interestingly, undissociated hydrogen atoms of phenol OH in each calix ring involve neighboring phenoxo oxygen in formation of O–H...O type intramolecular hydrogen bondings (Figure 2). The distances between proximal oxygen atoms are as follows: O4...O3 = 2.573, O5...O6 = 2.449, and O7...O8 = 2.411 Å, whereas O...O in free tetrathiacalix[4]arene **1** was reported to be 2.784 Å.¹¹ Judging from the O...O distances, the hydrogen bondings in the present Cu(II) complex are substantially stronger than those in **1**, because of the anionic charge of O_{phenoxo} as a stronger hydrogen acceptor, as well as the smaller framework of **5** than that of **1** to bring two phenolic oxygens closer as suggested by NMR and IR data.⁷

Notably, solvent molecules of different species, CHCl₃ and hexane, are encapsulated into each cavity of HL³⁻ and H₂L²⁻, respectively (Figures 1 and 2), which should be described as heteroditopic inclusion. To the best of our knowledge, such inclusion behavior has not been reported in dimeric calix[4]arenes connected by covalent or noncovalent bonds at the lower rim.¹² The torsion angles of distal aromatic planes (see the caption of Figure 2) indicates that HL³⁻ and H₂L²⁻ have a cavity of distinctively different shape. In general, the complementarity between the shapes of host and guest is one of the most important factors to determine the selectivity for host–guest binding.¹³ Therefore, the heteroditopic inclusion behavior should be originated from the difference in the cavity shape of two calix ligands to show the different affinity toward guest molecules.

Comparison of X-ray structure of present Cu(II) complex of **5** with one of tetrathia **1** (H₄L') contrasts the difference in the structural outcome of the thiacalix ligands with different numbers of sulfides. It has been reported that **1** formed a complex, [Cu₄L'₂], in which four Cu(II) ions are sandwiched between two calix-cones with apparent C_{4h} symmetry with an axis passing through the center of calix cones (Figure 3a).^{9,14} The structural identity of two calixarenes L'⁴⁻ leads to homoditopic inclusion of a CH₂Cl₂ molecule in each cavity. Two L'⁴⁻ provide four Cu(II) centers eight sets of O,S,O donors, resulting in O₄S₂ coordination environment around each Cu(II). By replacing the two distal –S– with –CH₂– in each calix in Figure 3a, while maintaining O₄S₂ environment around Cu(II) ions, one can predict that Cu(II) complex of dithia- **5** should be [Cu₂(H₂L)₂] (Figure 3b)⁸ with C_{2h} symmetry having two dianionic H₂L²⁻ to provide two Cu(II) ions four sets of O,S,O donors. From this view, rather unexpected is the formation of present [Cu₃(HL)(H₂L)(AcO)] complex without any symmetry to lead to heteroditopic inclusion (Figure 3c). This may be caused by excess use of Cu(II) ion, which might attack the phenol OH sites of [Cu₂(H₂L)₂] to rearrange the coordination core to make lower calix pivoting forward around one of Cu(II) ion (denoted as Cu_{piv}) and to distort the calix frameworks. On the other hand, all the phenoxo oxygens in [Cu₄L'₂] have already coordinated to two Cu(II) ions, hence it is difficult for excess Cu(II) ion, if any, to further occupy the O⁻ sites.

In summary, we note that the tricopper(II)-dithiacalix[4]ar-

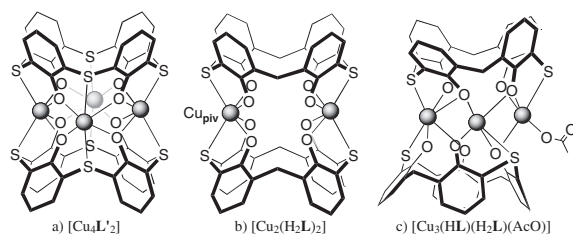


Figure 3. Schematic view of double-cone structures of Cu(II) complexes of thiacalix[4]arenes, H₄L and H₄L'. For clarity, protons on OH, negative charge on O⁻, *tert*-butyl groups, double bonds on aromatic ring are omitted.

ene (**5**) complex is the first example of any calix[4]arene dimer showing heteroditopic inclusion behavior, owing to the S–CH₂ alternate bridges of **5** and excess use of Cu(II).

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- Although Ref. 9 describes that [Cu₄(L')₂] has four-fold symmetry, careful examination of the crystallographic data (supplementary material) reveals that the complex has S₄ symmetry.