

## Topological Variation between Hexa- and Trithiacalix[6]arene–Copper(II) Complexes: From Sphere to Wheel by Reducing the Number of the Sulfur Bridges

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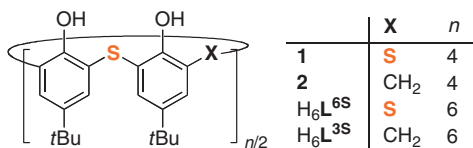
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Contrary to hexathiocalix[6]arene ( $H_6L^{6S}$ ) forming  $[Cu_{10}-(L^{6S})_2]$ -type spherical decacopper(II) complex, trithiacalix[6]arene ( $H_6L^{3S}$ ), in which three sulfur bridges of  $H_6L^{6S}$  are replaced with methylenes in an alternate manner, affords nanosized wheel-shaped octanuclear complex  $[Cu_8(H_2L^{3S})_4]$  consisting of four  $[Cu_2H_2L^{3S}]$  units.

Nanoscale architectures have attracted much attention because of their potential to serve as molecular devices, molecular machines, and functional materials.<sup>1</sup> One of the most effective strategies to construct the structure relies on noncovalent self-assembly based on precisely designed ligands to be spontaneously connected by metal ions.<sup>2</sup> In the efforts toward rational design of ligands to afford nanosized complexes, we have demonstrated that tetrathiocalix[4]arene (**1**)<sup>3,4</sup> as well as hexathiocalix[6]arene  $H_6L^{6S,6}$  (Scheme 1) are hopeful candidates because of their polydentate nature. For instance, ligand  $L^{6S6-}$  can include a multimetal core such as  $Cu^{II}_5$ ,  $Co^{II}_5$ , and mixed-metal  $M^{II}Ni^{II}_4$  ( $M = Mn, Co, \text{ and } Cu$ ) by adopting pinched-cone conformation with full participation of the bridging S and phenol O in coordination (for example of  $Cu^{II}_5$  core, see Figure 3a).<sup>5</sup> Moreover, two pentacopper(II) cores are further bridged by oxo and hydroxo ligands to form decacopper(II) cluster encapsulated in a nanosized sphere consisting of two hemispheres of  $L^{6S6-}$ .

Recently, we have provided a practical method for the preparation of dithiacalix[4]arene (**2**)<sup>7,8</sup> as well as trithiacalix[6]arene  $H_6L^{3S8,9}$  (Scheme 1) in which phenol units are bridged by methylene and sulfide groups in an alternate manner, which tempted us into a question how complex morphology is affected by reducing the number of sulfur donors. Herein, we report X-ray structure of trithiacalix[6]arene– $Cu^{II}$  complex having a completely different wheel-like topology rather than spherical morphology of decacopper(II)– $L^{6S6-}$  complex.

Reaction of trithiacalix[6]arene  $H_6L^{3S}$  and  $Cu(OAc)_2$  in 1:6 molar ratio in  $CH_2Cl_2/MeCN$  (1/1, v/v) at ambient temperature for 8 h, followed by crystallization from  $CHCl_3$ /hexane, gave deep red crystals of  $[Cu_8(H_2L^{3S})_4(H_2O)_4]$ .<sup>10</sup> X-ray structure of the complex showed a rectangular wheel structure with nanosized dimensions; ca.  $2 \times 2 \text{ nm}^2$  base and ca. 1.7 nm height



Scheme 1. Sulfur-bridged calix[n]arenes ( $n = 4$  and  $6$ ).

(Figure 1),<sup>11</sup> which are somewhat larger than those of decacopper(II) complex of  $H_6L^{6S}$  (Figure 1S). The wheel has a cavity with a bottleneck of ca.  $3 \times 3 \text{ \AA}^2$  rectangle, inside of which are included ca. 20 water molecules. In the crystal, the wheel complexes are packed to form a sheet in parallel with  $ab$  plane, which is layered in a staggered manner along the  $c$  axis to give continuous channels of wheel cavity (Figure 2S).

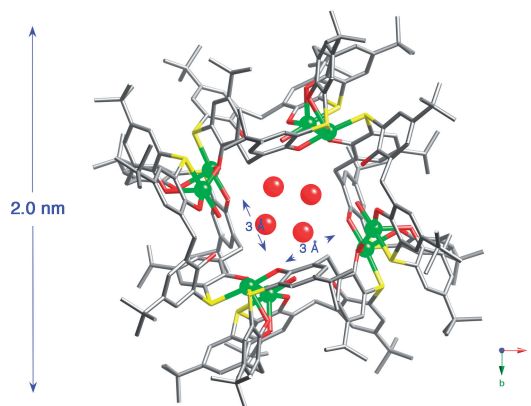


Figure 1. Crystal structure of the octacopper(II) complex,  $[Cu_8(H_2L^{3S})_4(H_2O)_4]$ , including water molecules. The carbons, oxygens, sulfurs, and coppers are in gray, red, yellow, and green, respectively.

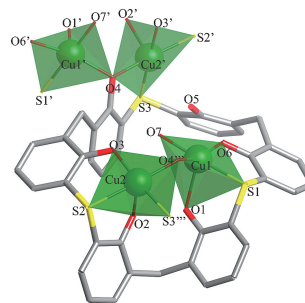
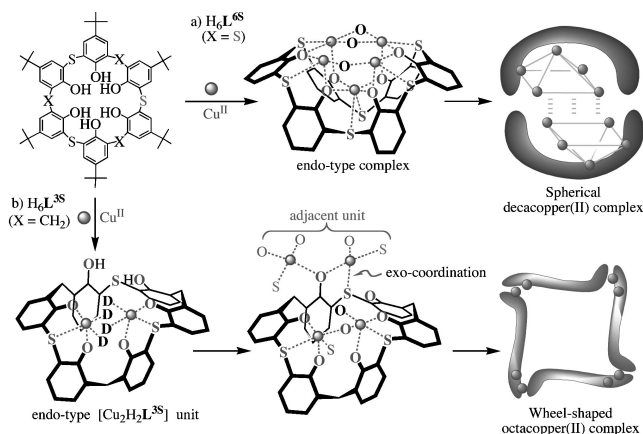


Figure 2. Dicopper(II) unit,  $[Cu_2H_2L^{3S}]$ , coordinating to adjacent dicopper(II) core. For clarity, *tert*-butyl groups and hydrogen atoms are omitted. Hydrogen bonds are formed between O1 and O2, O5 and O6.  $Cu1-S1$  2.3291(3),  $Cu1-O1$  2.265(8),  $Cu1-O6$  1.928(8),  $Cu1-O7$  1.967(8),  $Cu1-O4'''$  2.006(8),  $Cu2-S2$  2.3565(4),  $Cu2-S3'''$  2.3312(4),  $Cu2-O2$  2.207(7),  $Cu2-O3$  1.915(6),  $Cu2-O4'''$  1.979(7) Å. Atoms denoted prime (') and triple-prime (''') are related to their counterparts by the symmetry operations;  $(x + 1/2, -y + 1/2, -z + 1/2)$  and  $(-x + 1/2, y + 1/2, -z + 1/2)$ , respectively.



**Figure 3.** Possible complexation processes of a) hexathia  $H_6L^{6S}$  to decacopper(II) complex,  $[Cu_{10}(L^{6S})_2(\mu_3-O)_2(\mu_3-OH)_3(\mu-AcO)]_3$ , and b) trithia  $H_6L^{3S}$  to octacopper(II) complex,  $[Cu_8(H_2L^{3S})_4]$ . In the complex units, *p*-*tert*-butyl group and  $\pi$  electrons for benzene ring are omitted for clarity. D represents a donor atom of certain ligand species.

Since the crystal has crystallographic fourfold helical axis, the octacopper(II) complex can be divided into four crystallographically independent dicopper(II)- $H_2L^{3S4-}$  units ( $[Cu_2-H_2L^{3S}]$ , Figure 2). In this unit, two  $Cu^{II}$  ions ( $Cu1$  and  $Cu2$ ) are in a square-pyramidal coordination geometry with different sets of coordination atoms of  $O_4S$  and  $O_3S_2$ , respectively.  $Cu1$  is located at the center of the basal square consisting of  $S1$  and  $O6$  of  $H_2L^{3S4-}$ ,  $O7$  of water, and  $O4''$  of the adjacent  $H_2L^{3S4-}$  moiety with standard  $Cu-O$  and  $Cu-S$  distances (see caption of Figure 2).  $Cu1$  is further coordinated by  $O1$  located at axial position of the square pyramid with somewhat longer  $Cu-O$  distance.  $Cu2$  is placed in the bottom of a square-pyramid consisting of  $S2$ ,  $O3$ ,  $O4''$ , and  $S3''$  and coordinated by an apical  $O2$ , in which  $Cu-O$  and  $Cu-S$  distances are within standard ranges. The  $H_2L^{3S4-}$  takes a significantly distorted conformation, where sulfide ( $S3$ ) and phenol ( $O4$ ) moieties direct toward outside of the calix ring to coordinate to  $Cu1'$  and  $Cu2'$  of adjacent dicopper(II)- $H_2L^{3S4-}$  unit showing an exo-coordination fashion. On the whole,  $H_2L^{3S4-}$  ligand acts as a nonadentate ligand for  $Cu1$ ,  $Cu2$ ,  $Cu1'$ , and  $Cu2'$ . In addition, two hydrogen atoms remaining on the phenol oxygens of noncoordinating  $O5$  and weakly coordinating  $O1$  or  $O2$  (unassignable) form intramolecular hydrogen bondings  $O5 \cdots O6$  ( $=2.631(12)$  Å) and  $O1 \cdots O2$  ( $=2.428(3)$  Å), respectively.

Now, question arises why and how reduction of the numbers of bridging sulfides of hexathiocalix[6]arene  $H_6L^{6S}$  caused the different structural outcome. Given excess amount of  $Cu^{II}$  ion against a ligand,  $H_{6-n}L^{6Sn-}$  is able to coordinate to up to five  $Cu^{II}$  ions by full utilization of the six O and six S atoms with cooperative binding of three  $\mu$ -oxo ligands. In turn, each  $Cu^{II}$  ion is accommodated in a five or six coordination environment (Figure 3a).<sup>5</sup> Thus,  $H_{6-n}L^{6Sn-}$  acts as an endo-type ligand to end up with a spherical cluster morphology. On the other hand, Figure 2 is indicative of the precursor of octacopper(II) wheel complex to be dicopper(II) unit  $[Cu_2H_2L^{3S}]$ , because the number of  $Cu^{II}-H_2L^{3S4-}$  coordination bond between two units (3 bonds) is smaller than that inside a unit (6 bonds). Considering square-pyramidal coordination geometry of the  $Cu^{II}$  centers as exemplified by the decacopper(II) complex, each  $Cu^{II}$  in the precursor of

wheel complex should also have two donating atoms, D, at the equatorial positions (Figure 3b). In this situation, it is unlikely that the remaining free sulfide S and phenol O of  $[Cu_2H_2L^{3S}]$  coordinate to the third  $Cu^{II}$  center, which should further require additional ligation of D in order to give isolable complex. Rather, by adopting exo-directing conformation, the free O, S donor set should serve as the auxiliary ligand D for two  $Cu^{II}$  cores of neighboring  $[Cu_2H_2L^{3S}]$  precursor to form coordination bridges between the units. The fourfold repetition of the bridge formation between the units eventually builds up the wheel-shaped octacopper(II) complex.

In summary, we note regulation of the number of sulfur donors in the bridging moiety of calix[6]arene is an important factor to determine whether  $Cu^{II}$  centers settle inside the pocket of calix ligand or interconnect the ligands to lead to wheel topology in the self-assembly processes. In this context, structural study of  $Cu^{II}$  complexes with a series of thiocalix[6]arenes with different numbers of sulfide bridges at different positions<sup>9</sup> is a crucial task to obtain a strategy for rational design of a nano-sized molecular architecture.

## References and Notes

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- $[Cu_8(H_2L^{3S})_4(H_2O)_4]$ : A solution of  $Cu(OAc)_2$  (45 mg,  $2.4 \times 10^{-1}$  mmol) in  $CH_3CN$  (3 mL) was added to a solution of  $H_6L^{3S}$  (43.4 mg,  $4.2 \times 10^{-2}$  mmol) in  $CH_2Cl_2$  (3 mL). After stirring the reaction mixture at ambient temperature for 8 h, the solvent was evaporated to dryness. The residual solid was washed with water at three times and dried under vacuum. Recrystallization from  $CHCl_3$ -hexane gave deep red crystals of octacopper(II) complex (23.2 mg, 10.3% yield).
- Crystal data for  $[Cu_8(H_2L^{3S})_4(H_2O)_4] \cdot nH_2O \cdot 2hexane$  ( $n \approx 28$ ):  $O_{56}S_{12}Cu_8C_{264}H_{388}$ ,  $M_r = 5350.78$ , tetragonal, space group, *I4*,  $a = 21.3236(13)$ ,  $c = 35.507(3)$  Å,  $V = 16144.7(19)$  Å<sup>3</sup>,  $T = 220$  K,  $Z = 2$ ,  $D_{calcd} = 1.101$  g cm<sup>-3</sup>,  $\mu(Mo K\alpha) = 0.656$  mm<sup>-1</sup>,  $F(000) = 5688$ .  $\omega$ -scans, 59982 reflections measured ( $2\theta_{max} = 55^\circ$ ), of which 18570 were independent and 12110 were observed [ $I > 2\sigma(I)$ ], 896 refined parameters,  $R = 0.0484$ ,  $wR_2 = 0.1103$ . CCDC reference No. 284957.