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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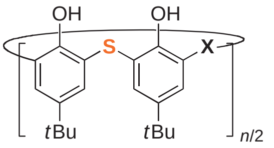
Contrary to hexathiacalix[6]arene ($H_6\mathbf{L}^{6S}$) forming $[Cu_{10}(\mathbf{L}^{6S})_2]$-type spherical decacopper(II) complex, trithiacalix[6]arene ($H_6\mathbf{L}^{3S}$), in which three sulfur bridges of $H_6\mathbf{L}^{6S}$ are replaced with methylenes in an alternate manner, affords nanosized wheel-shaped octanuclear complex $[Cu_8(H_2\mathbf{L}^{3S})_4]$ consisting of four $[Cu_2H_2\mathbf{L}^{3S}]$ units.

Nanoscale architectures have attracted much attention because of their potential to serve as molecular devices, molecular machines, and functional materials.[1] 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.[2] In the efforts toward rational design of ligands to afford nanosized complexes, we have demonstrated that tetrathiacalix[4]arene (**1**)[3,4] as well as hexathiacalix[6]arene $H_6\mathbf{L}^{6S}$[5,6] (Scheme 1) are hopeful candidates because of their polydentate nature. For instance, ligand $\mathbf{L}^{6S6-}$ can include a multimetal core such as $Cu^{II}{}_5$, $Co^{II}{}_5$, and mixed-metal $M^{II}Ni^{II}{}_4$ (M = Mn, Co, 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).[5] 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 $\mathbf{L}^{6S6-}$.

Recently, we have provided a practical method for the preparation of dithiacalix[4]arene (**2**)[7,8] as well as trithiacalix[6]arene $H_6\mathbf{L}^{3S}$[8,9] (Scheme 1) in which phenol units are bridged by methylene and sulfide groups in an alternate manner, which temped 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)–$\mathbf{L}^{6S6-}$ complex.

Reaction of trithiacalix[6]arene $H_6\mathbf{L}^{3S}$ 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 $[Cu_8(H_2\mathbf{L}^{3S})_4(H_2O)_4]$.[10] X-ray structure of the complex showed a rectangular wheel structure with nanosized dimensions; ca. 2 × 2 nm^2 base and ca. 1.7 nm height (Figure 1),[11] which are somewhat larger than those of decacopper(II) complex of $H_6\mathbf{L}^{6S}$ (Figure 1S). The wheel has a cavity with a bottleneck of ca. 3 × 3 $Å^2$ 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).



	X	*n*
1	S	4
2	CH_2	4
$H_6\mathbf{L}^{6S}$	S	6
$H_6\mathbf{L}^{3S}$	CH_2	6

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

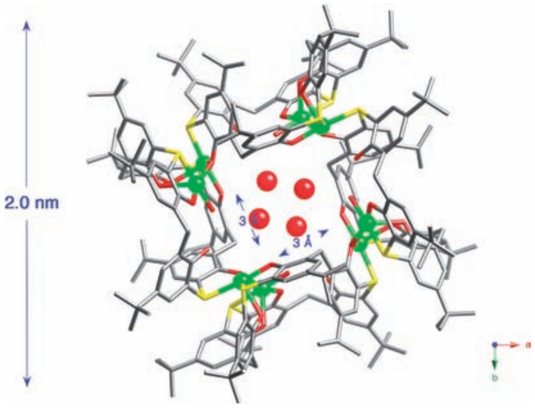


Figure 1. Crystal structure of the octacopper(II) complex, $[Cu_8(H_2\mathbf{L}^{3S})_4(H_2O)_4]$, including water molecules. The carbons, oxygens, sulfurs, and coppers are in gray, red, yellow, and green, respectively.

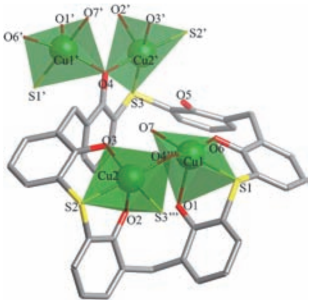


Figure 2. Dicopper(II) unit, $[Cu_2H_2\mathbf{L}^{3S}]$, coordinating to adjacent dicopper(II) core. For clarity, *tert*-butyl groups and hydrogen atoms are omitted. Hydrogen bonds are formed between O1 and O2, O5 and O6. Cu1–S1 2.3291(3), Cu1–O1 2.265(8), Cu1–O6 1.928(8), Cu1–O7 1.967(8), Cu1–O4‴ 2.006(8), 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.

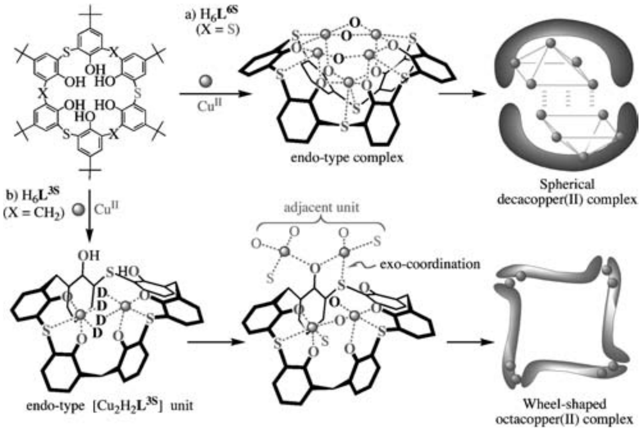


Figure 3. Possible complexation processes of a) hexathia $H_6\mathbf{L}^{6S}$ to decacopper(II) complex, $[Cu_{10}(\mathbf{L}^{6S})_2(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_3(\mu\text{-}AcO)]$, and b) trithia $H_6\mathbf{L}^{3S}$ to octacopper(II) complex, $[Cu_8(H_2\mathbf{L}^{3S})_4]$. In the complex units, *p-tert*-butyl group and π 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)-$H_2\mathbf{L}^{3S4-}$ units ($[Cu_2H_2\mathbf{L}^{3S}]$, 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 $H_2\mathbf{L}^{3S4-}$, O7 of water, and O4‴ of the adjacent $H_2\mathbf{L}^{3S4-}$ 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 $H_2\mathbf{L}^{3S4-}$ 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)–$H_2\mathbf{L}^{3S4-}$ unit showing an exo-coordination fashion. On the whole, $H_2\mathbf{L}^{3S4-}$ 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···O6 (=2.631(12) Å) and O1···O2 (=2.428(3) Å), respectively.

Now, question arises why and how reduction of the numbers of bridging sulfides of hexathiacalix[6]arene $H_6\mathbf{L}^{6S}$ caused the different structural outcome. Given excess amount of Cu^{II} ion against a ligand, $H_{6-n}\mathbf{L}^{6Sn-}$ 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 μ-oxo ligands. In turn, each Cu^{II} ion is accommodated in a five or six coordination environment (Figure 3a).[5] Thus, $H_{6-n}\mathbf{L}^{6Sn-}$ 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 $[Cu_2H_2\mathbf{L}^{3S}]$, because the number of Cu^{II}–$H_2\mathbf{L}^{3S4-}$ 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 $[Cu_2H_2\mathbf{L}^{3S}]$ 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 $[Cu_2H_2\mathbf{L}^{3S}]$ 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 thiacalix[6]arenes with different numbers of sulfide bridges at different positions[9] is a crucial task to obtain a strategy for rational design of a nano-sized molecular architecture.

References and Notes

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10 $[Cu_8(H_2\mathbf{L}^{3S})_4(H_2O)_4]$: A solution of $Cu(OAc)_2$ (45 mg, 2.4×10^{-1} mmol) in CH_3CN (3 mL) was added to a solution of $H_6\mathbf{L}^{3S}$ (43.4 mg, 4.2×10^{-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).

11 Crystal data for $[Cu_8(H_2\mathbf{L}^{3S})_4(H_2O)_4]\cdot nH_2O\cdot 2\text{hexane}$ ($n \approx 28$): $O_{56}S_{12}Cu_8C_{264}H_{388}$, $M_r = 5350.78$, tetragonal, space group, $I\bar{4}$, $a = 21.3236(13)$, $c = 35.507(3)$ Å, $V = 16144.7(19)$ Å^3, $T = 220$ K, $Z = 2$, $D_{calcd} = 1.101$ g cm^{-3}, μ(Mo Kα) $= 0.656$ mm^{-1}, $F(000) = 5688$. ω-scans, 59982 reflections measured ($2\theta_{max} = 55°$), 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.