

Calix[4]bis(thiacrown): Assembly of an Endocyclic Disilver(I) Complex and Exocyclic 3D Copper(I) Coordination Polymers

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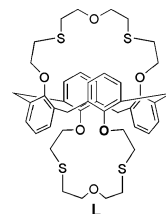
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Calix[4]bis(thiacrown-5) (**L**) with 1,3-alternating conformation was employed as a strong dinucleating ligand for the soft metal ions Ag^I and Cu^I. The reaction of **L** with AgPF₆ afforded a discrete endo-coordinated disilver(I) complex **1**, [Ag₂L](PF₆)₂. In contrast, mixed products (**2a** + **2b**) consisting of 3D networks were obtained from the reaction of **L** and CuI; **2b** linked with a Cu₄I₄ cubane unit was shown to generate photoluminescence, while **2a** linked with a Cu₂I₂ rhomboid unit does not.

Like the crown ethers,¹ calixarenes² are utilized as molecular building blocks for the design and construction of elaborated supramolecular systems. In particular, calixcrowns as the fusion of calixarene and crown ether units enable the divergent orientation of cavities of a size and nature sufficient to accommodate a variety of guests.³ Therefore, the research on mono- and binuclear complexes with diverse types of calixcrown derivatives has been a recent subject of interest.³ However, the reports of the preparation or crystal structure of the calix[4]bis(thiacrown) receptors, which can accommodate the soft metal ions in their individual cavity or provide the polymeric networks, are still sparse.⁴ We therefore focused our attention on the calix[4]-

bis(thiacrown) **L**^{4a} because the soft S donor has an affinity for soft metals such as Ag^I or Cu^I. Furthermore, numerous cuprous halide complexes ranging from the mononuclear species to long-chain polymers are luminescent.⁵



As was the case in our heteroleptic macrocyclic system reported previously,⁶ a possible strategy for the preparation of binuclear complexes with soft metal ions is the use of thiacrown rings because such systems frequently display exo orientation of the ring sulfur atoms. In the present Communication, two soft metal ions, Ag^I and Cu^I, have been employed in order to investigate how the resulting products are influenced by the use of either metal. The reaction of **L** with silver(I) hexafluorophosphate and copper(I) iodide, respectively, led to isolation of the disilver(I) complex **1** and two types of 3D copper(I) iodide networks (**2a** and **2b**), as depicted in Scheme 1. While **2a** incorporating a Cu₂I₂ linkage

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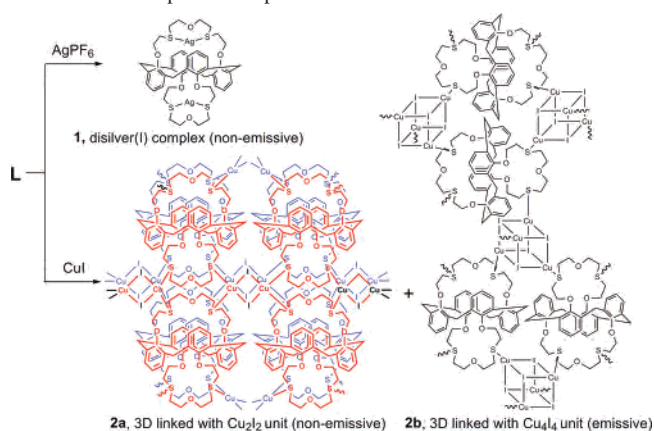
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Scheme 1 Compounds Prepared



was found to be nonemissive, the Cu_4I_4 -based **2b** exhibits photoluminescence. In the reaction of **L** with a mixture of Ag^+ and K^+ salts, no heterobinuclear complex was isolated in the solid state or detected in solution (Figure S5 in the Supporting Information).

L was synthesized as described previously by us.^{4a} Liquid–liquid diffusion of 2 equiv of AgPF_6 in water onto a dichloromethane solution of **L** on standing afforded the colorless crystalline product **1**. Single-crystal X-ray analysis revealed that **1** is a binuclear silver(I) complex of formula $[\text{Ag}_2\text{L}](\text{PF}_6)_2$ in which each metal atom is accommodated in the thiacycrown–ring cavities. In this complex, Ag1 coordination is completed by two strong Ag–S bonds. The environment of Ag1 is slightly different from that of Ag2 owing to the presence of a π interaction⁷ between Ag1 and C18 [$\text{Ag1}\cdots\text{C18}$ 2.623(6) Å] in the aromatic ring B. In fact, Ag1 is shifted by 0.2 Å outward from the S_2O_3 cavity and interacts with three C atoms (C17–C19) in the aromatic ring B (see Figure 1), leading to a η^3 -type cation $\cdots\pi$ interaction [$\text{Ag1}\cdots\text{C17}$ 2.983(6) Å and $\text{Ag1}\cdots\text{C19}$ 3.016(7) Å]. There are also η^2 -type interactions between Ag2 and both C11 and C12 [$\text{Ag2}\cdots\text{C11}$ 2.795(6) Å and $\text{Ag2}\cdots\text{C12}$ 2.811(6) Å] in the adjacent aromatic ring C. For each Ag atom, there are some additional weaker cation $\cdots\pi$ interactions, which range from 3.3 to 3.4 Å [$\text{Ag2}\cdots\text{C25}$ 3.374(6) Å and $\text{Ag1}\cdots\text{C4}$ 3.399(6) Å]. These latter observations are in accordance with additional stabilization of the disilver(I) complex **1** occurring with high ionophoricity. Long-range interactions between each Ag atom and the O donors (2.75–3.31 Å; van der Waals distance 3.2 Å) were also observed. By comparing the dihedral angles between two opposite aromatic rings of the 1,3-alternating calix[4] units in free **L** and in its disilver(I) complex **1**, we observe what may be considered to resemble a *chopsticks-type* π interaction (Figure S4 in the Supporting Information);⁴ namely, this dihedral angle shows a considerable change before (47.7° for **L**)^{4a} and after (A–C 15.65° and B–D 16.60° for **1**) complexation with Ag^+ . It is noteworthy that S–Ag–S bonds (117.6° and 119.4°) are highly bent toward the calix[4] unit because of the π interaction as well as the $\text{Ag}\cdots\text{O}$ (phenolic) interaction.

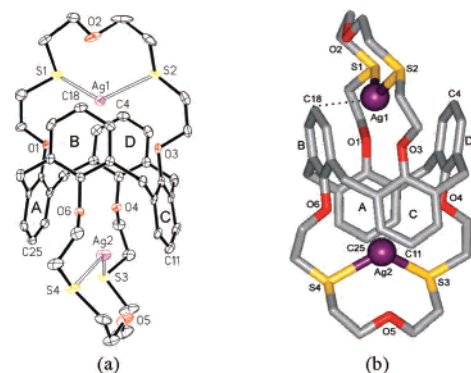


Figure 1. Crystal structure of **1**, $[\text{Ag}_2\text{L}](\text{PF}_6)_2\cdot\text{CH}_2\text{Cl}_2$: (a) ORTEP and (b) stick (90°-rotated) presentations. Noncoordinating anions and solvent are omitted.

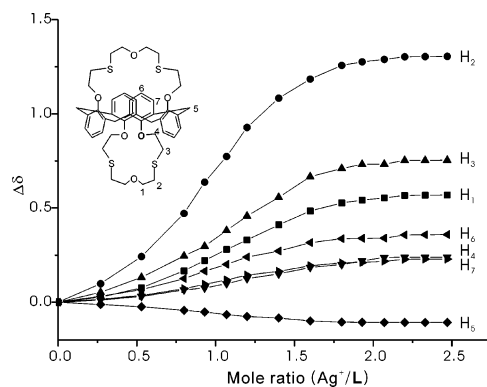


Figure 2. NMR titration of **L** with AgPF_6 in $\text{CD}_3\text{CN–CDCl}_3$ (1:1, v/v).

In an extension of the solid-state study, ^1H NMR titrations were performed in order to gain further insight about the complexation of **L** in solution. With AgPF_6 , the ^1H NMR titration curves unambiguously showed the formation of a 2:1 (Ag^+/L) complex (Figure 2). The relative order of magnitude of the chemical shift variation is $\text{H}_2 > \text{H}_3 > \text{H}_1 > \text{H}_{5,6} > \text{H}_{4,7}$, in keeping with Ag^+ being more strongly coordinated by S than O as also indicated by the solid-state structure.

Interestingly, the reaction of **L** in dichloromethane with 2 equiv of CuI in acetonitrile yielded two types of crystals: colorless bricks of **2a** and pale-yellow polyhedrons of **2b**, in which the topologies reflect different bridging CuI cluster units (see Scheme 1 and also Figures 3–5).

An X-ray analysis revealed that each product in the mixture constitutes a 3D network. The first of these, **2a**, was revealed to be a 3D polymeric array of formula $[\text{Cu}_2\text{L}_2]_n$ (Figure 3). The gross geometry of the 3D architecture for **2a** can be described as an interconnected layer. The rhomboid $\text{Cu–I}_2\text{–Cu}$ units are located at the center of four **L** molecules, and each cluster core is tetrahedrally coordinated by four S donors from four adjacent **L** molecules by Cu–S bonds to form a layer structure. Alternately, adjacent layers are interconnected by other rhomboid $\text{Cu–I}_2\text{–Cu}$ units to form a 3D array. The $\text{Cu}\cdots\text{Cu}$ distance [2.654(7) Å] is shorter than the van der Waals distance (2.8 Å) in the literature.⁸ The photoluminescent properties of the Cu_2I_2 rhomboid complex with N or P ligands depend on the $\text{Cu}\cdots\text{Cu}$ distances (i.e., less than the van der Waals distance:

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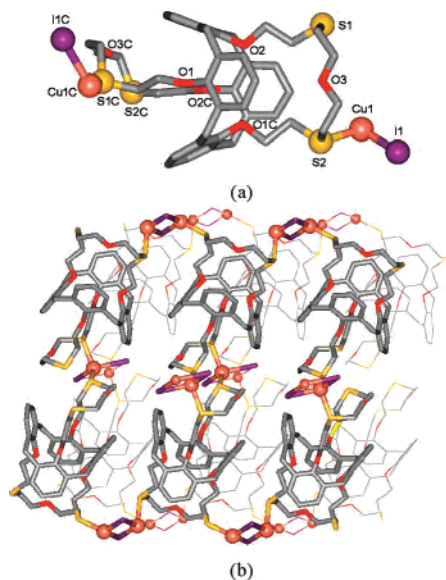


Figure 3. Crystal structure of **2a**, $[\text{Cu}_2\text{LI}_2]_n$; (a) core Cu_2LI_2 unit and (b) 3D network linked by $\text{Cu}-\text{I}_2-\text{Cu}$ rhomboid units.

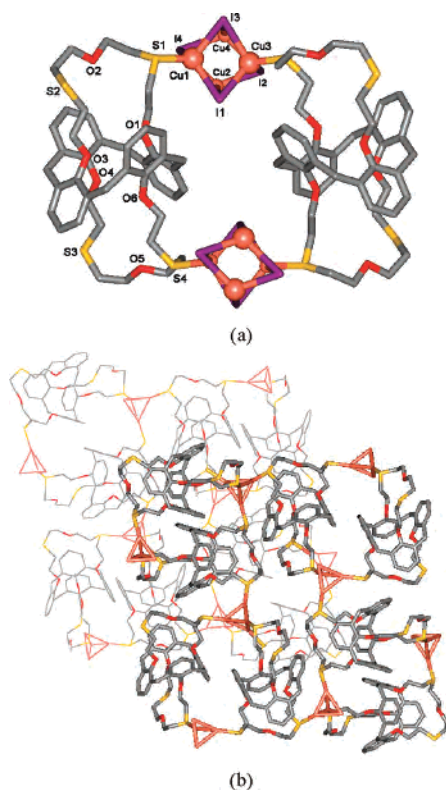


Figure 4. Crystal structure of **2b**, $[\text{Cu}_4\text{LI}_4]_n$; (a) core Cu_4LI_4 unit and (b) 3D network linked by Cu_4I_4 cubane units.

emissive).⁸ In the case of **2a**, however, no photoluminescence was observed.

As mentioned above, the X-ray analysis revealed that **2b** is also a 3D polymeric array. Its formula is $[\text{Cu}_4\text{LI}_4]_n$. The gross framework for **2b** can be described as an infinite 3D arrangement linked with the cubane-type Cu_4I_4 cores, whose geometry resembles a distorted cube with alternating vertices of Cu and I atoms. Each Cu atom in this cubane-type Cu_4I_4 unit is tetrahedrally coordinated to three μ_3 -I atoms and one S donor of **L**. Accordingly, four $\text{Cu}-\text{S}$ bonds between the

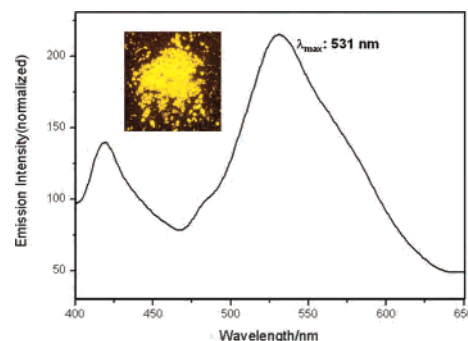


Figure 5. Solid-state emission spectrum of **2b** (excitation at 350 nm).

cubane core and the S donor (arising from four different ligands) occupy well-separated positions; these adjacent ligand molecules are arranged sparsely to minimize steric hindrance. The $\text{Cu}\cdots\text{Cu}$ distances (2.607–2.995 Å) are comparable with the van der Waals distance (2.8 Å). In contrast to **2a**, **2b** exhibits a bright-orange-yellow emission ($\lambda_{\text{ext}} = 531$ nm) in the solid state arising from the cluster-centered excited state with mixed halide-to-metal charge-transfer character.⁹ The researches about the photoluminescent properties of lanthanide metal complexes based on calixarene have been reported.¹⁰ To the best of our knowledge, this is the first case in which one product shows photoluminescence in 3D network complexes derived from calixarene derivatives.

In summary, the present paper reports the assembly and structural characterization of a discrete endo-type disilver(I) complex and a mixture of 3D copper(I) iodide products derived from a calix[4]bis(thiacrown). Two exo-coordinated CuI complexes in the mixed product are discriminated by the use of different linking units, namely, rhomboidic $\text{Cu}-\text{I}_2-\text{Cu}$ and cubane-type Cu_4I_4 units. Further investigation of the structure-dependent emitting properties of mixed products incorporating CuI complex species will be reported in due course.

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Supporting Information Available: X-ray crystallographic files in CIF format, synthetic procedures, NMR titrations, and analytical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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