



Short communication

Calix [4]-bis-monothiacrown-5 as a versatile building block for homo- and heterometallic coordination polymers



In-Hyeok Park, Ja-Yeon Kim, Eunji Lee, Huiyeong Ju, Seulgi Kim, Joon-Hwa Lee, Shim Sung Lee*

Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 52828, South Korea

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ABSTRACT

Exocoordination-based homonuclear and heteronuclear coordination polymers of calix [4]-bis-monothiacrown-5 (**L**) are reported. **L** reacts with Hg_2Cl_4 and affords a one-dimensional (1D) coordination polymer $[\text{L}(\mu\text{-Hg}_2\text{Cl}_4)]_n$ (**1**) linked by neutral square-type Hg_2Cl_4 clusters. A straightforward one-pot reaction of **L** with a mixture of HgCl_2 and KCl resulted in the isolation of a heteronuclear species $[(\text{K}_2\text{L})(\mu\text{-Hg}_3\text{Cl}_8)]_n$ (**2**) adopting a 1D polymeric structure in which the endocyclic dipotassium(I) complex cation units of **L** are linked by anionic open double-square type $(\mu\text{-Hg}_3\text{Cl}_8)^{2-}$ clusters. Both products form a pseudo 3D framework via interchain H-bonds and their topological analyses were also carried out.

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Sulfur-containing macrocycles (or thiamacrocycles) often exhibit the exocyclic coordination (metal binds outside the cavity) due to the inherent electron sufficiency and steric influence associated with the presence of the sulfur donors [1]. These include the family of calix [4]-bis-thiacrowns as a versatile platform which incorporates two thiacycrown loops in both sides of the calix [4]arene scaffold [2,3]. Related to the exocoordination of thiamacrocycles including calix [4]-bis-thiacrowns, a range of structural types from low to high dimensional coordination polymers as well as finite complexes have been introduced [2–4] and also reviewed by us [1].

We have been interested in the coordination networks based on calix [4]-bis-thiacrowns which form the endo- and/or exocoordination towards homo- and heterometallic species [3,5]. In the calix [4]-bis-thiacrown platform, we found that monothiacrown-5 [3] and dithiacrown-5 derivatives [2a] are promising candidates which form not only exocyclic complexes but also endocyclic ones due to the sulfur donor(s) as a bridgehead.

Our group also has established some strategies for the selective controlling of the endo- and exocoordination modes by changing anions and sulfur-to-sulfur distances in the dithiamacrocycles [4f,6]. In the later case, the dithiamacrocycles with the longer S...S distance tend to show a divergent exocoordination with soft metal ion or its cluster which leads the formation of continuous coordination species (Scheme 1a). We have reported some emissive one-dimensional (1D) networks of the endocyclic dipotassium(I) complex with calix [4]-bis-monothiacrown-5 (**L**) linked by the exocyclic copper(I) iodide cluster

(Scheme 1b) [3a]. Based on the HSAB concept [7] **L** might be considered to have a borderline character between hard and soft bases because of the O_4S donor-set. In fact, it was found that **L** shows slightly higher affinity towards potassium(I) than silver(I) both in solid and solution states [5].

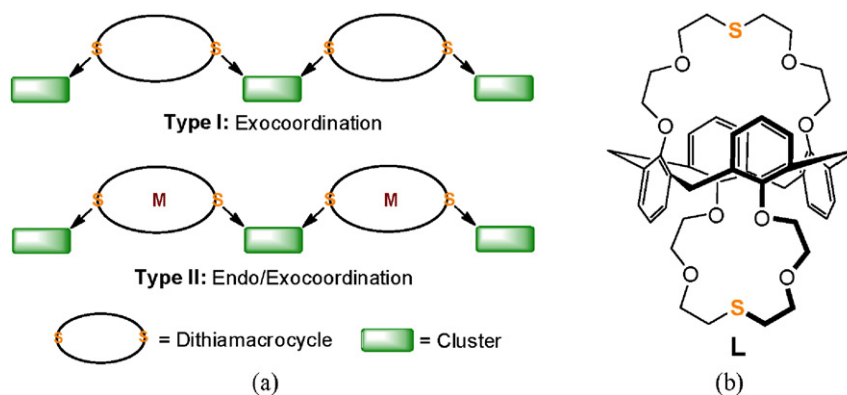
In addition to the metal ion bindings in the diverse coordination modes, coordinating anions play important roles in bridging or linking the complex units resulting in the formation of infinite structures. In our previous work, **L** forms a 2D infinite network with the endocyclic dipotassium(I) complex linked by an exocyclic mercury(II) iodide backbone [5]. The pseudo-halides such as cyanide and thiocyanate ions also show versatile coordinating/networking abilities due to their various coordination modes [8].

The continuing interest in calix [4]-bis-thiamacrocyclic platform and its expected diverse coordination modes due to the long sulfur-to-sulfur separation prompted us to investigate the fabrication of coordination polymers of **L**. In the present work, mercury(II) and potassium(I) were used as a soft/hard acids pair for the candidate of the exo- and endocyclic metal ions, respectively. As a counter ion, the chloride ion was employed due to its coordinating and bridging ability that might give the infinite products. Topological analyses of the products which show the pseudo 3D framework via intermolecular H-bonds were also carried out.

Calix [4]-bis-monothiacrown-5 (**L**) was prepared as reported by us previously [3a]. When HgCl_2 , as a thiaphilic soft acid, were reacted with **L** in methanol/dichloromethane, colourless crystalline product **1** was obtained after five days. Single crystal X-ray analysis confirms that **1** has a 1D polymeric arrangement with the formula being $[\text{L}(\mu\text{-Hg}_2\text{Cl}_4)]_n$ (Fig. 1a). Due to the inversion centre in the middle of two

* Corresponding author.

E-mail address: sslee@gnu.ac.kr (S.S. Lee).



Scheme 1. (a) Coordination modes and (b) calix [4]-bis-monothiacrown-5 (L).

Hg(II) atoms, the asymmetric unit in **1** contains half L molecule, one Hg(II) atom and two Cl atoms. In **1**, the calixcrown units with a 1,3-alternate conformation are linked by the square-shaped Hg₂Cl₄ cluster via Hg1-S1 and Hg1-O2 bonds in the exocoordination mode (Type I in Scheme 1) to generate the L-C-L-C (C: cluster) type chain structure. The Hg atom is five-coordinate being bound to one S atom and one O atom from L (Fig. 1b). The coordination sphere is completed by two bridging chloride ions (Cl1 and Cl1A) and one terminal chloride ion (Cl2) adopting a distorted square pyramidal geometry. The Hg—O bond distance [Hg1-O2 2.805(4) Å] is typical and the Hg—S bond distance [Hg1-S1 2.4727(13) Å] is also within the normal literature range for related system [9].

Recently, we have found that the endo- and exocoordination modes for some thiamacrocycles towards soft metal salts can be controlled by anions [6c,10]. For example, the halide anions with higher coordination affinity induce the soft metal ions locate outside the cavity to generate exocoordinated products. Consequently, the preferred formation of the 1D polymeric array in **1** via the exocyclic coordination mode of L is

mainly due to higher affinity of the chloride ion towards the mercury(II) to form the large cluster.

In the packing structure, it is found that the CH···Cl type H-bonds [11] (av. 2.85 Å) between adjacent chains (yellow dashed lines in Fig. 1c) links the chains to form a pseudo 3D framework (Fig. 1d). The details of the topological analysis for the pseudo 3D structure are discussed in the later part.

Having prepared and characterised the Hg₂Cl₄ cluster-bridged exocyclic coordination polymer of L, we continued to synthesise the heterometallic analogue. When HgCl₂ was changed to a mixture of HgCl₂ and KCl, a heterometallic 1D polymeric product **2** with the formula [(K₂L)(Hg₃Cl₈)_n] was obtained after two weeks (Fig. 2a). The asymmetric unit in **2** contains one L, two K(I) atoms, three Hg(II) atoms and eight Cl atoms.

In this case, two crystallographically different K1 and K2 atoms show similar coordination environment. They occupy the centres of two crown cavities to form a dipotassium(I) complex cation unit (K₂L)²⁺ via four K—O bonds (K1-O: 2.642(6)–2.804(7) Å, av. 2.712 Å and K2-

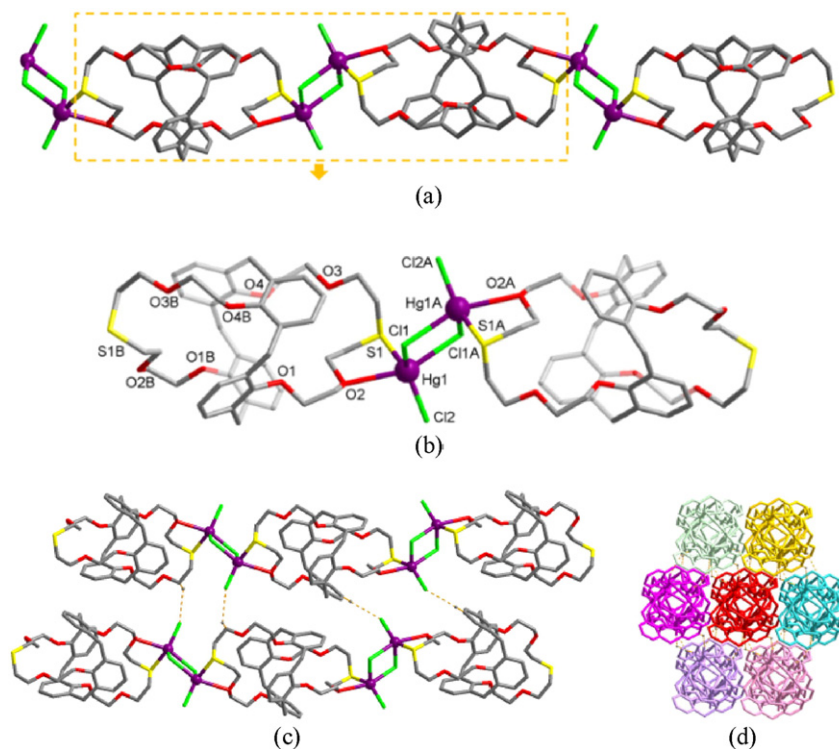


Fig. 1. Crystal structure of **1**, [L(μ-Hg₂Cl₄)_n]: (a) 1D polymeric chain, (b) core coordination unit, (c) interchain H-bonds (yellow dashed lines) and (d) packing structure showing a pseudo 3D framework. Symmetry codes (A): 2 - x, -y, 2 - z; (B): 1 - x, y, 1.5 - z.

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