Study of the Mechanism of Selective Recognition of *p-tert*-Butylcalix[4]thiacrown-5 for Organic Mercury(II) Compounds

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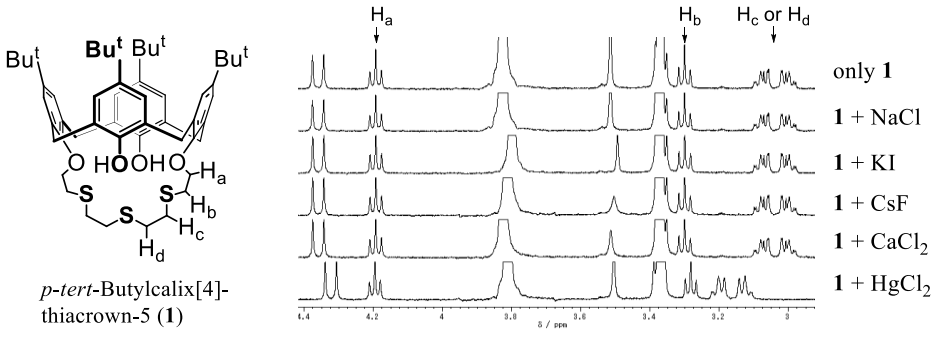
Keywords: *p-tert*-Butylcalix[4]thiacrown-5; Selective Trapping of Organic Mercury(II) Compounds; ^{1}H-NMR Titration; Binding Constant; Computational Simulation

We have synthesized calix[4]thiacrown derivatives[1] and investigated their recognition abilities to mercury(II) picrate dissolved in water solution by solid-liquid absorption experiment.[2] To research more easily the abilities, the behavior of ^{1}H-NMR chemical shifts of the thiacrown moieties in the coexistence of ion species is followed at present.[1] In this study, we investigated the affinity of the thiacrown moiety of *p-tert*-Butylcalix[4]-thiacrown-5 (**1**) to alkali, alkaline-earth metal, and some mercury(II) ions (Fig. 1). In addition, the binding constants of **1** to mercury(II) compounds, $HgCl_2$, $HgBr_2$, and $Hg(CH_3COO)_2$ were estimated. Finally, the recognition ability of **1** for mercury(II) compounds was discussed by using computational simulation.

As shown Fig. 1, the affinity of the thiacrown moiety of **1** was investigated to some inorganic compounds, NaCl, KCl, $CsCl_2$, $CaCl_2$, $HgCl_2$ in ^{1}H-NMR study. In the presence of the only $HgCl_2$, some chemical shifts of the thiacrown moiety of **1** moved into the low magnetic field. Furthermore, the binding constants were estimated to **1**-mercury(II) complexes using ^{1}H-NMR titration. The calix[4]thiacrown exhibited the highest affinity to $Hg(CH_3COO)_2$ among the three compounds, and the binding constant was 6.3 x 10^4 M^{-1}. That shows the calix[4]thiacrown trapped organic mercury(II) compounds specifically. The reason for the selective affinity of **1** to ones was discussed by the conformations predicted from the ^{1}H-NMR spectral analysis and computational simulation of **1**-mercury(II) complexes.



p-tert-Butylcalix[4]-thiacrown-5 (**1**)

Figure 1. ^{1}H-NMR spectra of **1** in the presence of various inorganic compounds.

1) T. Takimoto, H. Tsue, H. Takahashi, *Heterocycles*, **2014**, *88*, 911. 2) T. Takimoto, H. Tsue, R. Tamura, H. Sasaki, *Heterocycles*, **2015**, *90*, 842.