SELECTIVE ADSORPTION OF MERCURY(II) ION BY
INTERFACE

Tatsuya Takimoto,1* Hirohito Tsue,2 Rui Tamura,2 and Hideaki Sasaki1

1 Faculty of Pharmaceutical Sciences, Kobe Gakuin University, 1-1-3 Minatojima,
Chuo-ku, Kobe 650-8586, Japan. 2 Graduate School of Human and Environmental
Studies, Kyoto University, Yoshida-nihonmatsu, Sakyo-ku, Kyoto 606-8501,
Japan. e-mail: takimoto@pharm.kobegakuin.ac.jp

for heavy metal picrates has been studied. Of four heavy metal ions examined
herein, mercury(II) ion was selectively adsorbed, and the saturated adsorption
capacity reached to 7.3 ± 0.5 mg g⁻¹.

Even if the concentration of pollutants in aqueous environment is low, they will be accumulated in a
living being through biological concentration.1 For example, DDT of a high concentration was detected
from fish living in an outlying river in New York.2 Likewise, once heavy metal ions are released
unintentionally or accidentally into the environment, they may also be biologically accumulated in our
body via food chains. Therefore, it is very important to remove organic and inorganic pollutants
effectively from aqueous media.

In this context, we previously reported that the solid powder of *p*-tert-butylcalix[4]oxacrowns acted as an
efficient adsorbent for removing endocrine-disrupting chemicals from water through solid-liquid
adsorption phenomenon.3 More recently, we revealed that *p*-tert-butylcalix[4]thiacrown-5 2 (Figure 1)
involving three sulfur atoms in the crown moiety formed a complex with mercury(II) ion in organic
solvent.5 We anticipated that a combination of this nature of 2 and solid-liquid adsorption phenomenon
would be applicable to the removal of mercury(II) ion dissolved in water. As an eventual outcome, the
solid powder of 2 exhibited the selective uptake of mercury(II) ion among four heavy metal ions
examined in this study. Here we report the adsorption behavior of calix[4]thiacrowns 1 and 2 for heavy
metal ions.

This paper is dedicated to Professor Isao Kuwajima on the occasion of his 77th birthday.
Calix[4]thiacrowns 1 and 2 were prepared according to our reported procedure. First, batch adsorption experiments were carried out for a rough evaluation of the adsorption abilities of 1 and 2 for heavy metal ions. To an aqueous solution (5 cm³) containing 20 mg dm⁻³ heavy metal picrate (HgPic₂, PbPic₂, CdPic₂, or CoPic₂, where Pic indicates a picrate anion) in 50 cm³ stopped glass tubes was added 100 molar equivalent amounts of the solid powder of 1 or 2 with a particle size of <63 μm (Figure S1). After shaking at 300 rpm for 1 h at 25 °C, the suspensions were filtrated through a membrane filter, and the concentrations of the heavy metal picrates remaining in the filtrates were determined by UV measurements (Table 1).

Table 1. Removal percentages of heavy metal picrates by calix[4]thiacrowns 1 and 2

<table>
<thead>
<tr>
<th></th>
<th>HgPic₂</th>
<th>PbPic₂</th>
<th>CdPic₂</th>
<th>CoPic₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>(2.3%  )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8.1%</td>
<td>1%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>(23.6%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a determined by UV analysis. b determined by ICP analysis.

As can be seen from Table 1, the solid powder of 1 involving two sulfur atoms in the crown moiety showed no adsorption of all the heavy metal picrates examined herein. In contrast, 8.1% adsorption of mercury(II) picrate from the aqueous solution was observed by the solid powder of 2 containing three sulfur atoms, while no other heavy metal picrates were adsorbed. This experimental result is consistent with our recent report that the number of sulfur atoms in the crown moiety plays a crucial role in capturing mercury(II) ion, of which the complex is not formed with 1 but with 2 in organic solvent. As to the selectivity for mercury(II) ion, it is conceivable that the strongest soft acid character of mercury(II) ion among the examined heavy metal ions is responsible for the observed selective adsorption of mercury(II) ion on 2.

For more accurate evaluation of the adsorption abilities of 1 and 2 for mercury(II) picrate, the
concentration of the mercury(II) ion in the suspension was determined by means of ICP analysis. As a result, the solid powder of 1 was found to adsorb 2.3% of mercury(II) picrate, whereas the removal percentage by 2 reached to 23.6% (Table 1).

To gain a further insight into the adsorption abilities of 2 for mercury(II) ion, adsorption isotherm was created by changing the concentrations of mercury(II) picrate. Aqueous solutions (10 cm$^3$) of 4, 5, 8, 10, 20, and 40 mg dm$^{-3}$ mercury(II) picrate were placed in 50 cm$^3$ stopped glass tubes, each containing the solid powder of 2 (8.25 mg). The tubes were shaken at 300 rpm for 1 h at 25 °C, and the concentrations of mercury(II) ion in the suspensions were determined by ICP measurements. As shown in Figure 2a, a steep rise in the adsorption capacity was observed, indicating the high affinity of 2 for mercury(II) picrate at a solid–liquid interface probably using the crown moiety of 2 as an adsorption site.$^5$ The adsorption isotherm was analyzed by the Langmuir equation expressed as,

\[ W = aW_sC \]

where $W$ is adsorption capacity at equilibrium concentration $C$, and $W_s$ is saturated adsorption capacity, and $a$ is the Langmuir constant. From the Langmuir plot ($R^2 = 0.991$) shown in Figure 2b, the values of $W_s$ and $a$ were calculated to be 7.3 ± 0.5 mg g$^{-1}$ and 0.1 ± 0.1 mg$^{-1}$, respectively.

![Figure 2](image)

Figure 2. (a) Adsorption isotherm of mercury(II) ion on the solid powder of calix[4]thiacrown 2 at 25 °C and (b) the Langmuir plot

In conclusion, the present study has demonstrated that the solid powder of calix[4]thiacrown 2 is capable of selectively removing mercury(II) ion from an aqueous medium through solid-liquid adsorption phenomenon. Although the saturated adsorption capacity of 7.3 mg g$^{-1}$ by 2 is not necessarily high, we believe that the adsorbent function of 2 will be exerted more efficiently by fixing 2 onto resin, rather than the direct use of the solid powder. It is also likely that the oligomerization of 2 improves its adsorption
ability, as such enhancement is clearly and independently demonstrated by us and by Yilmaz and co-workers using a similar molecular system.\textsuperscript{3c,7} Investigation is in progress along this line.

**REFERENCE AND NOTES**


5. (a) Synthesis of cobalt(II) picrate: Picric acid (2.06 g, 8.99 mmol) was dissolved in Milli-Q water (50 cm\textsuperscript{3}) at 70 °C. To the solution was added cobalt carbonate (513 mg, 4.31 mmol). The solvent was evaporated under reduced pressure until the volume became about 5 mL. After filtration, the resultant yellow solid was recrystallized from Milli-Q water, filtrated, washed with cold Milli-Q water, and dried in vacuo to give cobalt(II) picrate (1.16 g, 43.0%) as a yellow solid. Anal. Calcd for C\textsubscript{12}H\textsubscript{4}CoN\textsubscript{6}O\textsubscript{14}·6H\textsubscript{2}O: C, 23.13; H, 2.59; N, 13.48. Found: C, 23.47; H, 2.54; N, 13.74; (b) Synthesis of cadmium(II) picrate: Picric acid (8.05 g, 35.1 mmol) was dissolved in Milli-Q water (200 cm\textsuperscript{3}) at 70 °C. To the solution was added cadmium carbonate (3.02 g, 17.5 mmol). After stirring for 100 min at 100 °C, the solvent was evaporated to dryness. To the resultant yellow solid was added boiled benzene. The solution was decanted, the residue was dried under reduced pressure. The resultant solid was recrystallized from Milli-Q water, filtrated, washed with cold water, and dried in vacuo to give cadmium(II) picrate (3.99 g, 41.1%) as a yellow solid. Anal. Calcd for C\textsubscript{12}H\textsubscript{4}CdN\textsubscript{6}O\textsubscript{14}·H\textsubscript{2}O: C, 24.57; H, 1.03; N, 14.33. Found: C, 24.21; H, 1.24; N, 14.30; (c) Synthesis of lead(II) picrate: Picric acid (7.98 g, 34.8 mmol) was dissolved in Milli-Q water (200 cm\textsuperscript{3}) at 70 °C. To the solution was added lead(II) acetate trihydrate (6.62 g, 17.5 mmol). After stirring for 4 h at 100 °C, the solvent was evaporated under reduced pressure until the volume became about 50 mL. After filtration, the resultant yellow solid was washed with 80 °C of Milli-Q water. The resultant solid was recrystallized from Milli-Q water, filtrated, washed with cold water and benzene, and dried in vacuo to give lead(II) picrate (3.78 g, 33.3%) as a yellow solid. Anal. Calcd for C\textsubscript{12}H\textsubscript{4}N\textsubscript{6}O\textsubscript{14}Pb·H\textsubscript{2}O: C, 21.15; H, 0.89; N, 12.33. Found: C, 21.11; H, 0.89; N, 12.16.

6. Opposite to our result, Yilmaz and co-workers reported that mercury(II) ion was captured by 1
through a liquid–liquid extraction experiment (see reference 7a). It is likely that the discrepancy is resulted from the difference in the experimental methods.