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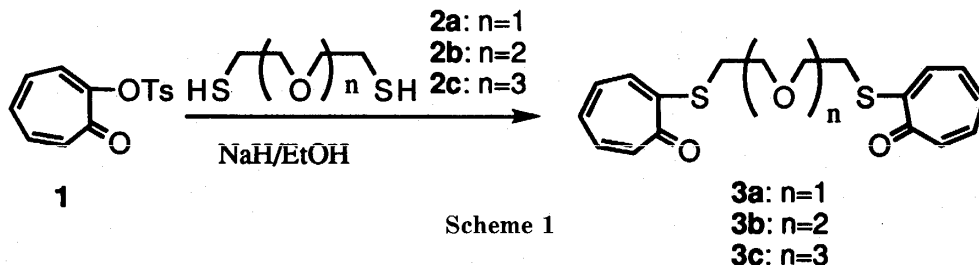
## Synthesis and Mercurophilic Properties of Bis(2-troponyl) Thioethers of Di-, Tri-, and Tetraethylene Glycols<sup>1)</sup>

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Condensation reaction of 2-(*p*-toluenesulfonyloxy)troponone with bis(2-mercaptoethyl) ethers of ethylene glycol homologues afforded bis(2-troponyl) thioethers of oligoethylene glycol derivatives. Due to an acyclic nature of polyethylene glycol moiety, they formed complexes with various metal ions. Reversible complexations with mercury salts were recognized.

Currently, we have been interested in synthesizing metal ion-capturing dithio-crown ether derivatives having troponoid pendants.<sup>2, 3)</sup> Particularly noteworthy are their reversible complexation behaviors with mercury(II) salts. According to the X-ray diffraction studies, there are two sites of coordination to indicate that the troponone ring is equally active as the complexation site to make the structure requirement quite flexible; the shortest homologue, 5-oxa-2,8-dithiabicyclo[7.4.1]tetradeca-9,11,13-trien-14-one, whose crown ring is not large enough to provide a space to include mercury(II) ion, was also reversibly mercuriphilic, since the mercury(II) ion is coordinated with the troponone carbonyl oxygen and the ethereal sulfur atoms. However, the most effective mercuriphile was shown to possess the structural feature, having at least five ethereal heteroatoms with the fitted cavity size for mercury.<sup>4)</sup> Thus, it is interesting to investigate the mercuriphilic properties as well as the general metallophilic properties of acyclic analogues, although the selectivity of the acyclic system towards metal salts should well be lower than the cyclic counterparts. Herein described are the confirming results of these predictions with the podant-type dithioether derivatives having a 2-troponyl pendant.

When 2-(*p*-toluenesulfonyloxy)troponone (**1**) was treated with bis(mercaptoethyl) ether (**2a**) and sodium hydride by means of a microfeeder under high dilution conditions, a 1 : 2-condensate (**3a**), diethylene glycol bis(2-troponyl) thioether, was obtained in 90% yield. Similarly, triethylene and tetraethylene glycol bis(2-troponyl) thioethers (**3b** and **3c**) were



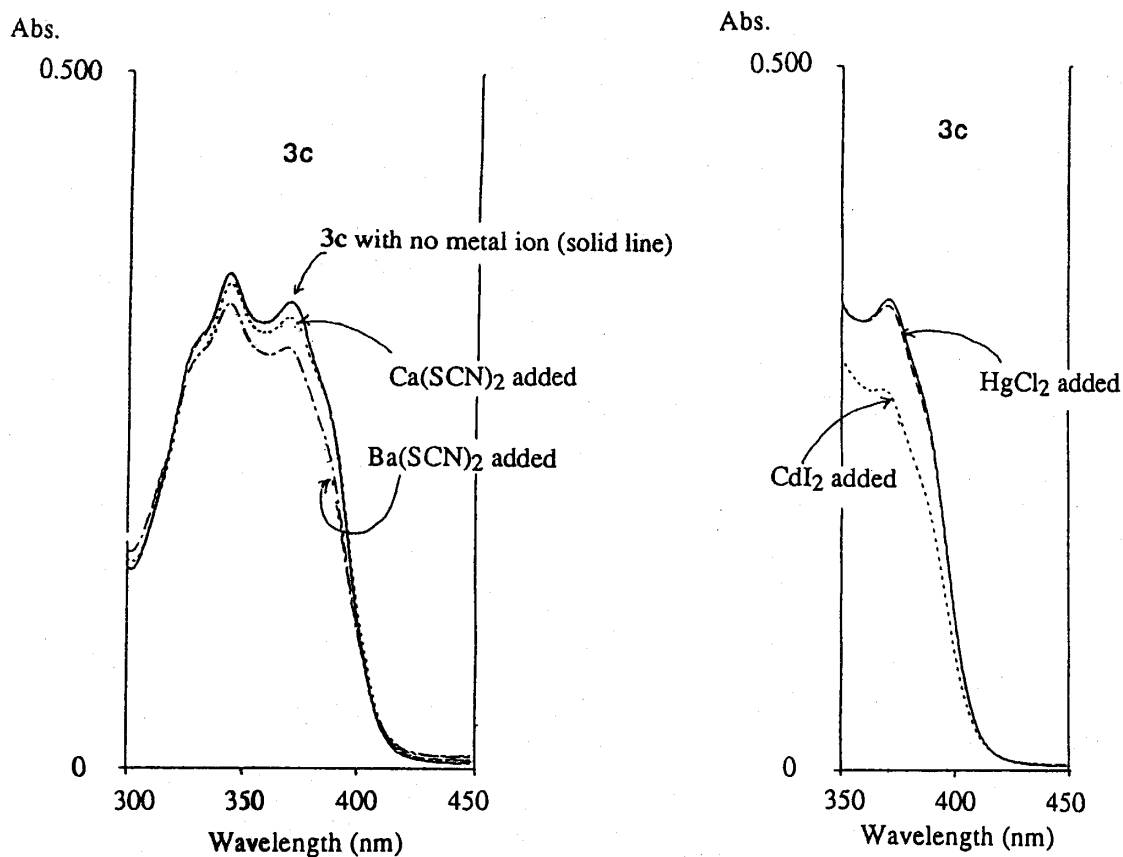
**Table 1** UV-spectral analysis of complex formation of **3a-c** with several metal ions.

Compds.	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Ba <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Hg <sup>2+</sup>
<b>3a</b>	—	—	—	—	—	++	—	—	—	—
<b>3b</b>	—	—	—	—	—	++	—	—	—	—
<b>3c</b>	—	—	—	—	—	++	++	—	++	—

obtained in 92 and 95% yields, respectively.

The UV-spectral analysis of complexations of **3a** to **3c** with various metal salts was carried out; the most pronounced change in the absorption spectra was observed with calcium ion, and then, barium and cadmium salts showed changes with **3c**. On the other hand, <sup>1</sup>H NMR spectral screening experiments suggested a complexation with mercury ion. No other metals revealed a change in the chemical shifts by addition of metal salts. Fig. 1 shows the detected UV-spectral changes of **3c** caused by addition of several metal salts; other than the illustrated, examined metal ions were lithium, sodium, potassium, ammonium, magnesium, and zinc ions with **3a-c** (Table 1). Remarkable feature was that, although UV-spectral change of **3c** upon complexation with mercury(II) ion was not significant, the change was visible in NMR spectroscopy as shown in Fig. 2. Indeed, it extracts and transfers mercury ion selectively.<sup>5)</sup>

It is noteworthy that mercury ion was transported with all **3a-c**, but the longer the chain length, the faster the rate of transportation. To form pentadentated complexes with mercury (II) ion, two and one tropone carbonyl oxygens of **3a** and **3c** should respectively take a part,

**Fig. 1** The UV spectral changes of **3c** by additions of metal ions.

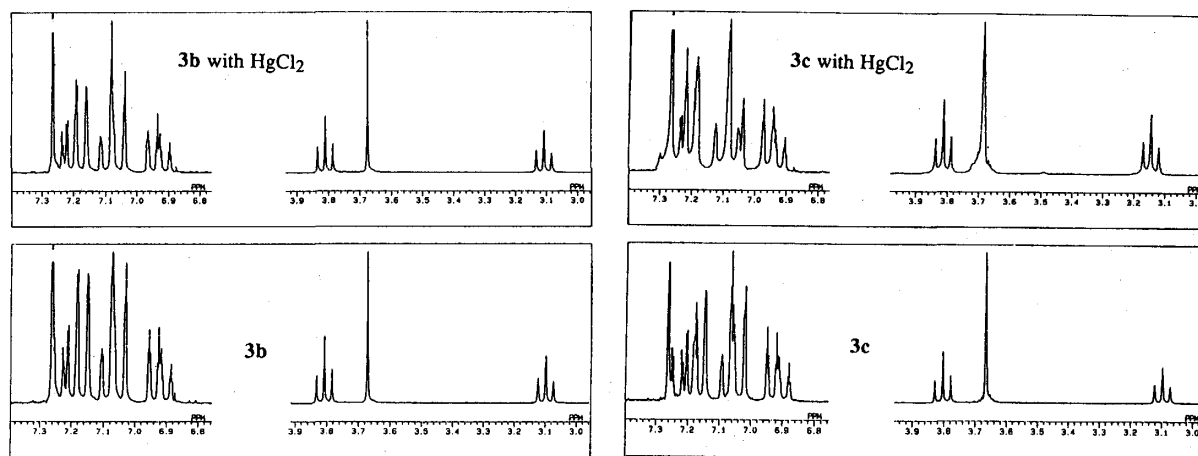


Fig. 2 The NMR spectral change of **3b** and **3c** by additions of mercury(II) ion.

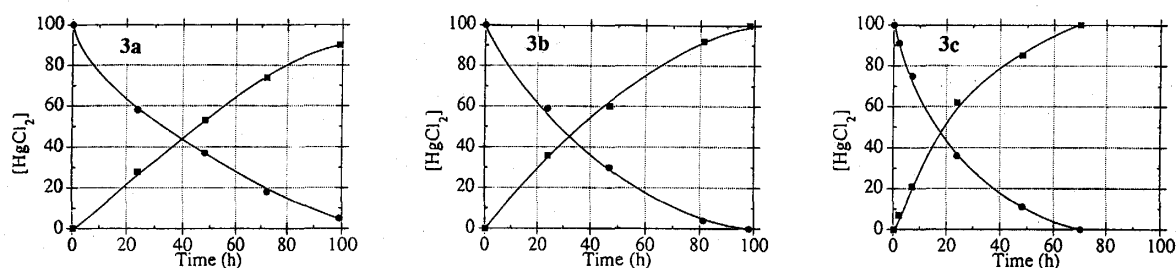


Fig. 3 Transportation experiments of  $\text{HgCl}_2$  with **3a-c**.

while **3c**, having five ethereal heteroatoms, may not use the carbonyl oxygen for coordination with the mercury(II) salt. This may be a reason why the longer chain showed a facilitated transportation behavior. Therefore, it is strongly desirable to synthesize higher homologues to investigate the transportation experiments in near future. As **3a-c** possess larger conformational mobility than the cyclic counter parts, the selectivity towards metal ions could be diminished when compared with the cyclic crown derivatives, and there might be a possibility that the metal salts other than mercury(II) salt could also be transported. However, the experimental results still showed a marked difference; zinc and cadmium salts were not transported and remained all in original solutions.

Detailed discussions will be subject of a forthcoming full paper.

## References

- 1) This paper has been dedicated to Dr. Tetsu Fujii, Professor Emeritus, of Kyushu University in the occasion of his retirement.
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- 4) The X-ray diffraction studies of various mercury (II) complexes have been extensively carried out. The results are subjects of joint publications with other research groups.
- 5) The apparatus, U-type cell, was the same to that used in the previous studies.