

	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
a:	-NHCOCH <sub>2</sub> Ph	CH <sub>2</sub> CCl <sub>3</sub>	
b:	-NHCOCH <sub>2</sub> Ph	-CH(Ph) <sub>2</sub>	H
c:	-NHCOCH <sub>2</sub> Ph	-CH(Ph) <sub>2</sub>	Cl
d:	-NHCOCH <sub>2</sub> Ph	CH <sub>2</sub> CCl <sub>3</sub>	H
e:	-NHCOCH <sub>2</sub> Ph	CH <sub>2</sub> Ph	H

Scheme 1.

The formation of the 6-membered cepham was rationalized by intramolecular addition to a double bond in 5-exo fashion,<sup>14</sup> rearrangement and hydrogen abstraction.<sup>9</sup>

Further studies in order to stop the reaction in penam stages are under way.<sup>15</sup>

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- Cephams **2e**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 0.92 (d, J=7 Hz, 3H), 1.25 (m, 1H), 2.37, 2.93 (AX, J=13 Hz, 2H), 4.46 (s, 2H), 4.56 (d, 1H), 5.0-5.5 (m, 4H), 6.77-7.50 (m, 11H); IR (KBr) 3400, 1763, 1728, 1666 cm<sup>-1</sup>; MS (m/z) 440.
- Cephams **2e** was given in low yield using other U.V. lights such as 3014 Å and 3467 Å. Mercaptan **1e** was unstable at higher temperature.<sup>4</sup>
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- In fact, we once obtained a penam but failed to reproduce.

### Unusual Stability Increment of Ag(I)-Podand Complexes

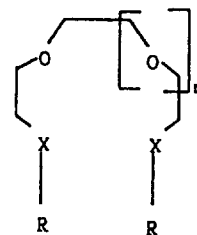
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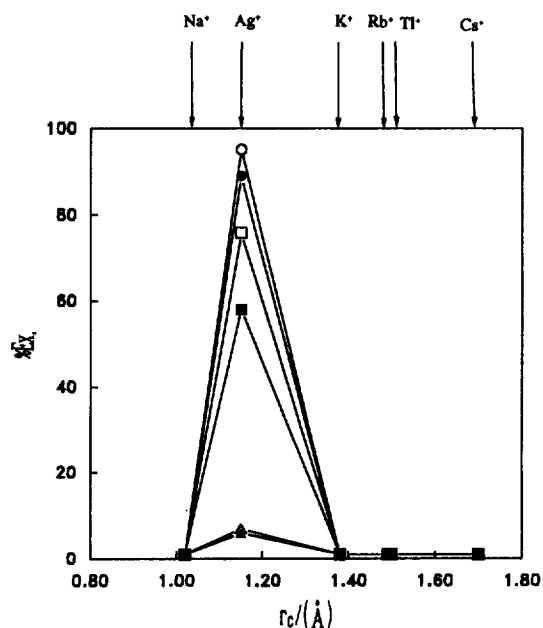
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The oligoethylene glycol derivatives with aromatic donor groups at both ends, called podands can be obtained simply and cheaply.<sup>1-3</sup> Some podands containing larger aromatic groups with heterodonor atoms wrap themselves around the cations such as Na<sup>+</sup> and Rb<sup>+</sup> ion in a helical manner to make pseudocavity in solid and solution states.<sup>1,2</sup> But no experimental evidence was observed that the simple aromatic groups, such as phenyl group, take place in such a stacking interaction to enhance the selectivity for given cations. Furthermore, the podands possessing the sulfur-oxygen mixed donor atoms have been much less frequently studied.<sup>3</sup> Under these circumstances, we have designed some podands possessing sulfur donor atoms in ether chain and simple aromatic moieties, such as phenyl (Ph) or benzyl (Bz) groups at both ends, which could be expected as the strong ionophores for Ag(I) ion rather than alkali metal ions.

The influence of the flexibility of aromatic end groups on the stacking interaction have not investigated carefully. Thus, in this study we confirm the conformational change by incorporation of methylene spacing groups to the aromatic end groups, which favors the formation of pseudocavity and increases the stability.



Ph <sub>2</sub> O <sub>4</sub>	: n=1; X=O; R=phenyl,	Ph <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	: n=1; X=S; R=phenyl
Bz <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	: n=1; X=S; R=benzyl,	Ph <sub>2</sub> O <sub>3</sub>	: n=2; X=O; R=phenyl
Ph <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	: n=2; X=S; R=phenyl,	Bz <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	: n=2; X=S; R=benzyl



**Figure 1.** Plots of cation radii vs. %Ex. of cation picrate from aqueous to chloroform layer with  $Bz_2O_2S_2$  (○),  $Bz_2O_3S_2$  (●),  $Ph_2O_2S_2$  (□),  $Ph_2O_3S_2$  (■),  $Ph_2O_4$  (△) and  $Ph_2O_5$  (▲).

## Results and Discussion

**Syntheses of Podands.** All of the podands were prepared by the reaction of the corresponding dichloride with phenol, thiophenol or benzylmercaptane in the presence of KOH in ethanol or tetrahydrofuran. The detailed procedures are described in experimental section.

**Solvent Extractions.** Extractions of some univalent cation picrates including alkali metal, Ag(I) and Tl(I) ions from aqueous to chloroform layer have been performed using podands as extractants. According to Figure 1, any other cations were not extracted by the podands used except Ag(I) ion. In the previous work,<sup>4</sup> the podands which consisted of an oligoethylene glycol and two quinolinylxy groups showed maximum extraction efficiency for K(I) ion among alkali metal ions as result of changing the length.

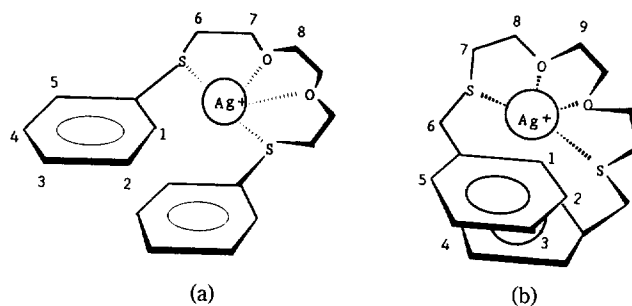
The podands with four ligating sites ( $O_2S_2$  or  $O_4$ ) have an enhanced extractability for silver picrate compared to the corresponding podands with five ligating sites ( $O_3S_2$  or  $O_5$ ), demonstrating the negative contributions of an extra donor oxygen. This could be said that the increase of entropy of ligand decrease the extractability for the smaller ions, such as silver(I) ion.

The  $Bz_2O_2S_2$ , possessing methylene spacer groups between sulfur and the phenyl group, gave the overall increase in extraction of silver(I) picrate compared to  $Ph_2O_2S_2$  and  $Ph_2O_3S_2$ , respectively. Since, only the existence of the methylene bridge between sulfur and phenyl group led to better extraction character, the stability and conformational change on complexation were necessary. Thus, it will be discussed in following sections by the results of the potentiometry and NMR.

**Stability Constants of Ag(I)-Podand Complexes ( $AgL^+$ ).** To determine the stability constants of the complexes with Ag(I) ion, the potentiometric titrations were very

**Table 1.** Stability Constants of Podand Complexes with Silver(I) Ion in Methanol at 25.0°C

Podand	log K	Podand	log K
$Ph_2O_4$	>2	$Ph_2O_5$	>2
$Ph_2O_2S_2$	5.92	$Ph_2O_3S_2$	5.50
$Bz_2O_2S_2$	8.01	$Bz_2O_3S_2$	7.37



**Figure 2.** Proposed conformation of (a)  $Ph_2O_2S_2-Ag(I)$  and (b)  $Bz_2O_2S_2-Ag(I)$  ion complexes in solution.

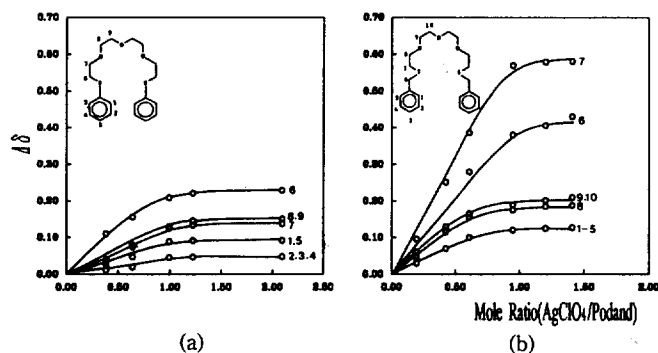
successful because the Ag(I)-ISE responded nearly Nernstian in methanol and the curve-fitting program, KINFIT<sup>8</sup> gave the quite reasonable results in accuracy. Log K values for the 1 : 1 interaction of some podands with silver perchlorate were obtained and listed in Table 1. A binding stoichiometry of Ag(I) ion per a given podand was also confirmed from NMR titration described in the following section and the extraction coefficient,  $\log K_{ex}$  in our previous work.<sup>9</sup>

The substitutions of the sulfur atoms for oxygens in ether chains produce the dramatic effect on log K. As expected, the sulfur atoms acts as a soft base to enhance the stability toward the Ag(I) ion, classified as a soft acid.<sup>5,10</sup>

Comparing the stability constants of Ag(I) ion with corresponding  $O_2S_2$ - and  $O_3S_2$ -type podands, the larger podands showed lower stability than the smaller one, in spite of the increment in the donor atom number. Generally, glyme-type ionophores show an increase in their complexing abilities with change in the number of donor atom.<sup>6,7</sup> But the  $Q_2O_n$ -type ( $Q$ =quinoline,  $n=3, 4$  or  $5$ ) podands showed similar affinity toward Ag(I) ion and no maximum selectivity with  $n$  number.<sup>8</sup>

More interesting thing is that the podands with benzyl moieties, such as  $Bz_2O_3S_2$  and  $Bz_2O_2S_2$  showed much higher stabilities (70 to 100 times) than their phenyl analogues,  $Ph_2O_3S_2$  and  $Ph_2O_2S_2$ . The only differences, as mentioned in extraction part, is the existence of a methylene group between sulfur and phenyl group. What happened to the benzyl group upon complexation?

The enhancement of stability constant caused by the methylene spacing group, which can be ascribed to the higher flexibility of benzyl containing-podands and the maximum affinity as a result of the presence of methylene spacing group strongly suggests that these kinds of complexes are stabilized not only by a spherical wrapping effect same as glymes, but also by an oriented face-to-face association structure as a part of  $\pi$ - $\pi$  stacking<sup>11,12</sup> interaction between aromatic moieties shown in Figure 2(b).



**Figure 3.** The plots of chemical shift changes *vs.* mole ratio of (a)  $\text{AgClO}_4/\text{Ph}_2\text{O}_3\text{S}_2$  and (b)  $\text{AgClO}_4/\text{Bz}_2\text{O}_3\text{S}_2$  in  $\text{AC-d}_6/\text{DMSO-d}_6$  (7 : 3 v/v). The numbers indicate the nonequivalent protons represented in Figure 2.

**NMR Titrations.** When a donor atom coordinates a central cation the chemical shifts of neighboring protons generally tend to shift downfield.<sup>2,10</sup> From the result of NMR titrations shown in Figure 3, every resonances shifted downfield upon complexation and both ligands form 1 : 1 complexes with  $\text{Ag(I)}$  ion.

Since the chemical shifts of methylene protons of ether chain depend mainly on the strength of the interaction between nearest neighboring donor atoms and cation.  $\text{Bz}_2\text{O}_3\text{S}_2$  and  $\text{Bz}_2\text{O}_3\text{S}_2$ , which have favorable selectivity for  $\text{Ag(I)}$  ion in Figure 1 have shown fairly large shift in  $\text{H}_6$  and  $\text{H}_7$ . But  $\text{H}_6$  in  $\text{Ph}_2\text{O}_3\text{S}_2$  shifts a little bit larger than any other protons. These results suggest that sulfur donor atoms participate in coordination stronger than any other oxygens in both cases.

The remarkable difference of the chemical shift for proton neighboring sulfur atoms ( $\text{H}_6$  in  $\text{Ph}_2\text{O}_3\text{S}_2$  and  $\text{H}_7$  in  $\text{Bz}_2\text{O}_3\text{S}_2$ ) may be ascribed to the pseudo-cycle formation on complexation of  $\text{Bz}_2\text{O}_3\text{S}_2$  with silver shown as in Figure 2. This could be understood by considering that the increase of flexibility by the length and conformational freedom are responsible for the formation of a pseudocycle more easily than phenyl groups do as illustrated in Figure 2(a) and 2(b). Thus, this unusual behavior is due to a helical conformation of the complex with partial stacking of the benzyl groups.

Our previous work<sup>2</sup> and other workers<sup>4,13</sup> have recently reported from the upfield shift of aromatic proton that the  $\text{Na(I)}$  or  $\text{K(I)}$  ion complexes of some podand with quinoline end groups and oxygen donor atoms are stabilized by the pseudo-cycle conformation similar to crown ether. In this work, however, no upfield shifts of aromatic proton were observed on complexation. The origin of the drastic increment of stabilities may arise from the  $\pi$ - $\pi$  interaction of aromatic moieties<sup>12,14</sup> between both benzyl group. An alternative proposal is that the aromatic ring is participating in a  $\pi$ -interaction with silver(I) ion.<sup>15</sup> However, the examination of molecular model appears to disfavor the possibility of  $\pi$ -interaction with silver(I) ion. Thus, it may be explained by considering that the inductive effect of strong sulfur-silver(I) ion interaction on aromatic proton is large enough to cancel the upfield shifts of aromatic protons due to the stacking interaction.

Successful development of the acyclic host molecules capable of high silver ion selectivity would be of interest to wor-

kers in separation and molecular-design chemistry. Taking the extraction, NMR and stability results into account, the aromatic stacking stabilizations are able to keep their conformation on a pseudocyclic structure like a crown ether. Thus, the introduction of aromatic moieties and spacing groups to the molecular design of effective acyclic ionophore could be an important factor.

## Experimental

**General.** The  $^1\text{H-NMR}$  spectra were recorded with a Bruker AW80 NMR spectrometer. The chemical shift was determined from TMS, and  $\text{AC-d}_6/\text{DMSO-d}_6$  (7 : 3 v/v) mixed solvent was used in NMR titrations. The IR spectra were recorded with a Hitachi 270-50 spectrophotometer. The UV-visible spectra were recorded on a Beckman DU70 spectrophotometer.

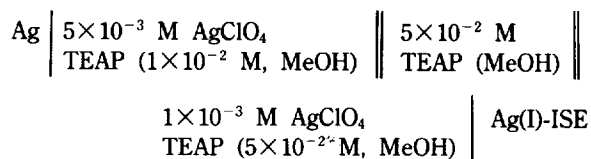
**Syntheses of Podands. 1,11-bis(thiophenoxy)-3,6,9-trioxaundecane ( $\text{Ph}_2\text{O}_3\text{S}_2$ ) and 1,9-bis(thiophenoxy)-3,6-trioxaundecane ( $\text{Ph}_2\text{O}_2\text{S}_2$ ).** 1,11-Dichloro-3,6,9-trioxaundecane (25 mmol) or 1,8-dichloro-3,6-dioxaoctane (25 mmol) dissolved in 25 mL ethanol was added dropwise within 30 min and under stirring to refluxing solution of thiophenol (55 mmol) and  $\text{KOH}$  (55 mmol) in 100 mL ethanol. The mixture was refluxed for 20 h and was then allowed to cool to room temperature. After filtration of the precipitate and the solvent was removed by distillation under vacuum, chloroform was added to the viscous oil to dissolve. In order to separate the unreacted, the mixture was extracted several times with dilute  $\text{NaOH}$  and washed with distilled water. The organic layer was concentrated by distillation under vacuum. Chromatography on silica gel with chloroform : ethanol (98 : 2 v/v) gave the pure products.

**1,11-Bis(mercaptobenzyl)-3,6,9-trioxaundecan ( $\text{Bz}_2\text{O}_3\text{S}_2$ ) and 1,9-Bis(mercaptobenzyl)-3,6-dioxaoctane ( $\text{Bz}_2\text{O}_2\text{S}_2$ ).** Benzylmercaptane (20 mmol) and  $\text{NaOH}$  (20 mmol) were dissolved in boiling THF (100 mL). Under refluxing condition, 1,11-dichloro-3,6,9-trioxaundecane (10 mmol) or 1,9-dichloro-3,6-dioxaoctane (10 mmol) in 50 mL THF was added dropwise for 30 min. The mixture was then stirred for another 1 h. The procedure for workup was the same for  $\text{Ph}_2\text{O}_3\text{S}_2$ . The product was purified by chromatography on silica gel (eluent : *n*-hexane/ethylacetate, 4 : 1 v/v).

**NMR Titrations.** The chemical shifts of each protons among podands were determined by a frequency counter within an error of  $\pm 0.2$  Hz, relative to TMS zero locking. The use of  $\text{AC-d}_6/\text{DMSO-d}_6$  mixtures as the solvents in NMR titration was based on the solubility considerations. A sample tube containing a few milligrams of podand in a known volume of solvent was first loaded into the probe and spectrum was taken. The sample was then unloaded, added to the sample tube with a small amount of the solid salt, reloaded into the probe, and another spectrum was taken. This process was repeated until no significant change was observed in successive spectra. Usually seven to ten spectra were taken for each of the experiment. The concentrations of podands were held constant at about  $5 \times 10^{-3}$  M and salt concentration varied from 0.0 M to approximately 0.01 M.

**Potentiometry.** All potentiometric titrations were done with  $\text{Ag}^+$ -ISE (Orion 94-16) in anhydrous methanol. The double junction type reference electrode was used. The ge-

neral construction of the cell used for the measurements was as follows.



Titration were carried out in an all-glass cell thermostated to  $25 \pm 0.1^\circ\text{C}$ . Titrant was added from 5 to 10 mL microburets calibrated. The data were analyzed, using KINFIT4<sup>8</sup> to fit the calibration curves for calculating the stability constants.

**Extractions.** The chloroform solution of the podand (5.0 mL,  $3.0 \times 10^{-3}$  M) and the aqueous solution of cation picrate (5.0 mL,  $3.0 \times 10^{-3}$  M) were placed in a volumetric flask, and the flask was shaken in thermostated incubator for 30 min at  $25 \pm 0.2^\circ\text{C}$ . The concentration of univalent cation picrate in the water phase was determined from its absorption at 356 nm.

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## Thermal Reduction of *arachno*-S<sub>2</sub>B<sub>7</sub>H<sub>8</sub><sup>-</sup> to *hypho*-S<sub>2</sub>B<sub>7</sub>H<sub>10</sub><sup>-</sup> and Synthesis of New Metalladithiaborane Clusters Derived From *hypho*-S<sub>2</sub>B<sub>7</sub>H<sub>10</sub><sup>-</sup>.

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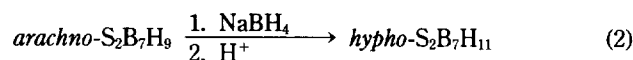
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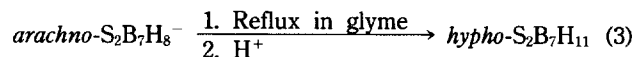
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Previously *hypho*-S<sub>2</sub>B<sub>7</sub>H<sub>11</sub> was obtained from either the reaction of BH<sub>3</sub>·THF or NaBH<sub>4</sub> with *arachno*-6,8-S<sub>2</sub>B<sub>7</sub>H<sub>8</sub><sup>-</sup> or *arachno*-6,8-S<sub>2</sub>B<sub>7</sub>H<sub>9</sub> in moderate yield as shown in Eq. 1 and 2.<sup>1,2</sup> The formation of *hypho*-S<sub>2</sub>B<sub>7</sub>H<sub>11</sub> was viewed as involving an initial interaction between the Lewis acid BH<sub>3</sub> and the base borane anion, followed by a cluster rearrangement.



In this study we found that *arachno*-S<sub>2</sub>B<sub>7</sub>H<sub>8</sub><sup>-</sup> has been thermally transformed to the corresponding *hypho*-S<sub>2</sub>B<sub>7</sub>H<sub>10</sub><sup>-</sup> in excellent yields.<sup>3</sup> Thus, the reaction was carried out during a period of overnight at refluxing condition and subsequent protonation gave the corresponding *hypho*-S<sub>2</sub>B<sub>7</sub>H<sub>11</sub> in a good yield. It has been noted that the conversion of *arachno*-S<sub>2</sub>B<sub>7</sub>H<sub>8</sub><sup>-</sup> to *hypho*-S<sub>2</sub>B<sub>7</sub>H<sub>10</sub><sup>-</sup> was varied with the solvent used and the best conversion was observed when *arachno*-S<sub>2</sub>B<sub>7</sub>H<sub>8</sub><sup>-</sup> was refluxed in glyme solvent.



This procedure makes *hypho*-S<sub>2</sub>B<sub>7</sub>H<sub>11</sub> compound one of the most readily available thiaborane intermediate which can be used for further syntheses without purification. This dithiaborane has been identified by its mass spectrum, <sup>1</sup>H and <sup>11</sup>B-NMR spectra, and by comparison with an authentic sample.<sup>2</sup>

This high yield preparation of the *hypho*-S<sub>2</sub>B<sub>7</sub>H<sub>10</sub><sup>-</sup> dithiaborane enabled us to use it for a convenient synthesis of a variety of new metalladithiaboranes. Thus, we have now investigated these possibilities and report here the syntheses and structural characterizations of a unique series of nine- and ten-vertex dithiaborane clusters derived from *hypho*-S<sub>2</sub>B<sub>7</sub>H<sub>11</sub>.

Treatment of *hypho*-S<sub>2</sub>B<sub>7</sub>H<sub>10</sub><sup>-</sup> with Cp(CO)<sub>2</sub>FeCl in glyme at reflux temperature overnight resulted in the formation of an orange-yellow complex I (24% yield), under the condition of dry column chromatography on silicagel in *n*-hexane. Exact mass measurement supports the proposed composition of C<sub>5</sub>H<sub>5</sub>FeS<sub>2</sub>B<sub>7</sub>H<sub>8</sub>.<sup>4</sup> The <sup>11</sup>B-NMR spectrum shows evidence