

## Molecular design of crown ethers. 18.<sup>1</sup> Cationextractability and selectivities of seleno-13- to 14-crown-4

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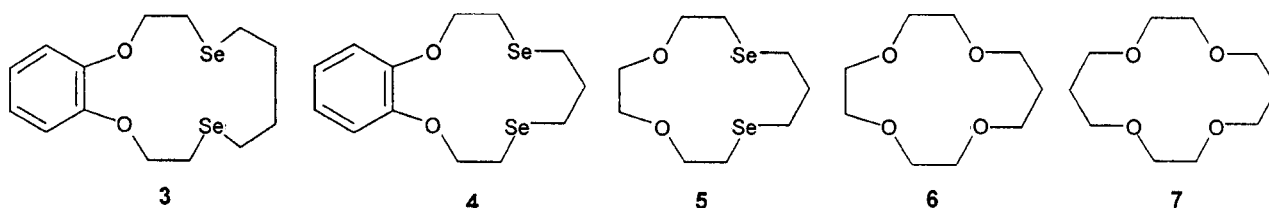
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Three seleno-crown-4 derivatives have been prepared and their cation binding abilities and selectivities with alkali and heavy metal ions have been evaluated by solvent extraction of aqueous metal picrates to show the highest  $\text{Ag}^+$  extractability for novel benzo-selena-14-crown-4 (2,3-benzo-7,12-diselena-1,4-dioxacyclotetradecane-2-ene) over any other crown ethers.

**Keywords**      Seleno crown ethers, extractability, selectivities

In the past three decades, enormous effort has been devoted to the synthesis of a wide variety of crown ethers and complexation thermodynamics with crown ethers to enhance the cation-binding ability and selectivity,<sup>2</sup> but effort in selenocrown ethers was inadequate.<sup>3,4</sup> Selenocrown ethers have higher cation-binding ability with some of the transition metal and the heavy metal cations

than common crown ethers,<sup>5-8</sup> however, few of the study examples about the solvent extraction of alkali and heavy metal ions with selenocrown ethers have been reported.<sup>8</sup> In the present paper, we synthesized a series of seleno-crown-4 derivatives, 2,3-benzo-7,12-diselena-1,4-dioxacyclotetradecane-2-ene (**3**), 2,3-benzo-7,11-diselena-1,4-dioxacyclotridecan-2-ene (**4**), and 1,5-diselena-8,11-dioxacyclotridecane (**5**) shown in Chart 1, and evaluated their cation binding abilities with aqueous alkali ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) and some heavy ( $\text{Ag}^+$ ,  $\text{Tl}^+$ ) metal picrates. The results obtained are compared with the relevant 1,4,7,10-tetraoxacyclotridecane (**6**) and 1,4,8,11-tetraoxacyclotetradecane (**7**) data in Table 1. It is of our specific interest to examine the binding ability and selectivity of soft cations by crown-4 derivatives **3**—**7**.



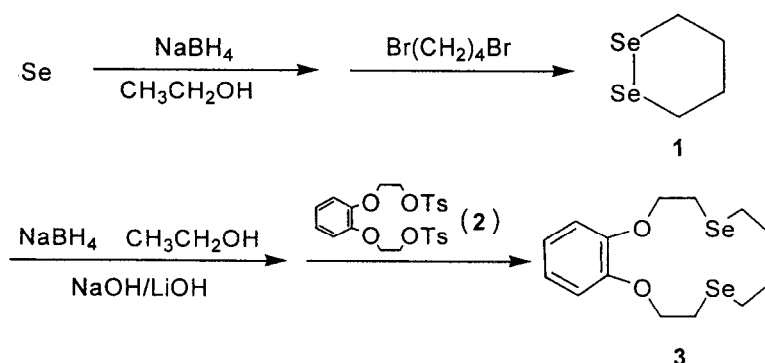
All crown-4 derivatives were synthesized by using a mixed base, *i. e.*  $\text{LiOH}/\text{NaOH}$  as selectable template. The key intermediate 1,2-diselenocyclohexane (**1**), was prepared by the reaction of potassium borohydride as reductive agent with selenium and 1,4-dibromoterepane in alcohol in 10.5% lower yield (Scheme 1) than that of 1,2-diselenocyclopentane.<sup>13</sup> It is known that synthesiz-

ing cyclocompound demands the two ends of open link chain compounds to be near enough to bond. The bigger the ring of cyclocompounds is, the less the possibility of the two ends of chain to bond is. Typically, the novel **3** was synthesized in 37% yield by the reaction of **1** with *o*-bis(tosyloxyethoxy)benzene (**2**).

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## Scheme 1



The extractabilities (% Ex) obtained for **3**, **4**, and **5** are shown in Table 1, along with those of **6** and **7**. Also listed are the selected relative cation selectivities of  $\text{Li}^+/\text{Na}^+$  and  $\text{Ag}^+/\text{Tl}^+$ , calculated from the distribu-

tion ratio of metal ion between the organic and aqueous phases:  $D_M = [\text{M}^+]_{\text{org}} / [\text{M}^+]_{\text{aq}} = \% \text{Ex} / (100 - \% \text{Ex})$ .

Table 1 Solvent extraction of aqueous metal picrates with selenacrown-4<sup>a</sup>

Ligand	Extractability <sup>b</sup> (%)					Selectivity <sup>c</sup>	
	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Ag}^+$	$\text{Tl}^+$	$\text{Li}^+/\text{Na}^+$	$\text{Ag}^+/\text{Tl}^+$
<b>3</b>	0.41	6.17	0.51	93.9	0.31	0.06	4950
<b>4</b>	0.10	5.14	0.41	86.0	<i>e</i> )	0.02	
<b>5</b>	6.33	11.9	8.18	87.0	15.0	0.50	39.7
<b>6<sup>d</sup></b>	0.80	3.80	1.25	8.74	6.13	0.20	1.47
<b>7<sup>d</sup></b>	13.9	0.98	0.58	4.58	2.49	16.3	1.88

*a*, Temperature  $25 \pm 1^\circ\text{C}$ ; aqueous phase (5 mL): [picrate] =  $1 \times 10^{-4}$  M; organic phase ( $\text{CH}_2\text{Cl}_2$ , 5 mL): [crown ether] =  $1 \times 10^{-3}$  M. *b*, Defined as percent picrate extracted into the organic phase. Average of two independent runs; error < 3% of the reported value. *c*, Relative cation selectivity determined by the distribution ratio of metal ion between the organic and aqueous phase. *d*, Ref. 9. *e*, Not detected.

As shown in Table 1, all crown-4 derivatives exhibit higher extractabilities for  $\text{Na}^+$  over  $\text{Li}^+$  and  $\text{K}^+$ , except for **7**, which has favorable orientation of donor atoms in ring for the size-matched  $\text{Li}^+$  over larger alkali metal ions.<sup>9</sup> Particularly, **3** and **4** possess higher selectivity of  $\text{Na}^+$  than the rest crown ethers in Table 1. One possible explanation for this result would be that the diameters of **3**, **4** and **5** are matched with that of  $\text{Na}^+$ , so they show lower extractability of  $\text{Li}^+$  and  $\text{K}^+$  than that of  $\text{Na}^+$ . The altered spatial arrangement and reduced electron density of donor atoms through incorporation of the benzo substituent in **3** and **4** lead to higher cation selectivities compared with corresponding unsubstituted crown ethers, and in the meanwhile, the ring effect becomes chief factor to the % Ex for cations. The host compounds **3**, **4** and **5** gave startling extractivities for  $\text{Ag}^+$ , and un-

usual selectivity for  $\text{Ag}^+/\text{Tl}^+$ .  $\text{Ag}^+$  cation is soft, so is selenium donor. The interaction of soft selenium donors with soft  $\text{Ag}^+$  cation leads to the largest enthalpic gain ( $\Delta H^\circ$ ) and the large, but much smaller entropic loss ( $T\Delta S^\circ$ )<sup>4</sup> which is in sharp contrast to the complexation thermodynamic behavior of hard  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Tl}^+$  cations.

It is concluded that, in the crown-4 series, **3** possesses higher solvent extractability and selectivity to  $\text{Na}^+$ , and all selenacrown-4 have unusually high solvent extractability to  $\text{Ag}^+$  and selectivity to  $\text{Ag}^+/\text{Tl}^+$ .

## Experimental

Melting points, measured with an XT-4 apparatus, are uncorrected.  $^1\text{H}$  NMR spectra were recorded on a DE-OL-DX 200  $^1\text{H}$  NMR spectrometer at 200 MHz in

$\text{CDCl}_3$  solution. Infrared and ultraviolet spectrum were recorded on Shimadzu IR-435 and Shimadzu UV-2401/PC instruments, respectively. The result of elementary analysis was obtained on Perkin-Elmer-2400C instrument.

Alcohol was dried and distilled from Na. Picrates of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ag}^+$  were prepared as reported.<sup>10,11</sup> Thallium picrate was prepared from picric acid and thallium nitrate ( $\text{TlNO}_3$ ). Picric acid (3.4 g, 15 mmol) was dissolved in water (400 mL), to which aqueous solution of thallium nitrate (4.0 g, 15 mmol) was added slowly and the mixture was stirred for 10 min at room temperature. The precipitate was recrystallized twice from water to give 4.3 g (66%) of thallium picrate.

*o*-Bis(tosyloxyethoxy)benzene (**2**) was prepared as reported.<sup>12</sup>

Benzo-selena-13-crown-4 (**4**) and selena-13-crown-4 (**5**) were prepared as reported.<sup>13</sup>

**1,2-Diselenocyclohexane (1)** Selenium powder (4.74 g, 60 mmol) and potassium borohydride (2.36 g, 42 mmol) were poured into a flask under  $\text{N}_2$ , and a little of absolute alcohol was dropped into the flask. After the initial reaction had subsided, the rest absolute alcohol (210 mL) was added fast, and the mixture was stirred and heated at reflux for 2 h with  $\text{N}_2$  passing into the liquid in order to dissolve the selenium and expel  $\text{H}_2\text{Se}$ .<sup>14</sup> A solution of 2.4 mL (20 mmol) of 1,4-dibromotetane in 30 mL of absolute alcohol was dropped into the brownish red solution, and the mixture was heated at reflux for other 10 h. After cooling, the solid was filtered off and solvent was vacuum distilled. The residue was extracted with tetrahydrofuran and the extract was concentrated in vacuum to give a reddish orange stringy liquid **1** (0.5 g, 10.5%).  $\delta_{\text{H}}$ : 3.037 (t,  $J = 4$  Hz, 4H,  $2 \times \text{CH}_2$ ), 2.095 (t,  $J = 3$  Hz, 4H,  $\text{CH}_2\text{CH}_2$ ).

**Benzo-selena-14-crown-4 (3)** 1,2-Diselenocyclohexane (0.2 g, 0.93 mmol),  $\text{NaBH}_4$  (0.15 g, 4.0 mmol),  $\text{NaOH}$  (0.16 g, 4.0 mmol),  $\text{LiOH}$  (0.07 g, 3.0 mmol) were added to a flask under  $\text{N}_2$ , and 20 mL of absolute alcohol was added to the stirred mixture. After the mixture was heated at reflux for 1 h, a solution of **2** (0.506 g, 1.0 mmol) in 30 mL of absolute alcohol was dropped into the transparent solution, and stirring

was continued for 17 h at reflux. The cooled mixture was filtered, and the solvent was vacuum distilled to give a yellowish oil which was purified by column chromatography on silica (100—200 mesh, benzene) and then crystallized from alcohol to give **3** (0.13 g, 37%) as colorless crystal: mp 107.5—108°C.  $\nu_{\text{max}}$ : 1591, 1504 (s, Ar), 1252, 1213, 1122, 1061 (s, C—O)  $\text{cm}^{-1}$ .  $\delta_{\text{H}}$ : 6.89—6.81 (m, 4H, ArH), 4.39 (t,  $J = 5$  Hz, 4H,  $2 \times \text{OCH}_2$ ), 3.02 (t,  $J = 7.5$  Hz, 4H,  $2 \times \text{OCH}_2\text{CH}_2\text{Se}$ ), 2.93 (t,  $J = 5$  Hz, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.90—1.83 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ ). Anal.  $\text{C}_{14}\text{H}_{20}\text{O}_2\text{Se}_2$ . Calcd: C, 44.44; H, 5.29. Found: C, 44.32; H, 5.66.

Solvent extraction was performed as described previously.<sup>10,15</sup>

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