

# **Synthesis of Some Selenacrown Ethers and the Thermodynamic Origin of Their Complexation with C60**

Yu Liu,<sup>\*</sup> Jian-Rong Han, Yan-Li Zhao, Heng-Yi Zhang, and Zhong-Yu Duan

*Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China*

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\*Corresponding author. Fax: +86-22-23503625.

E-mail: yuliu@public.tpt.tj.cn

## Abstract

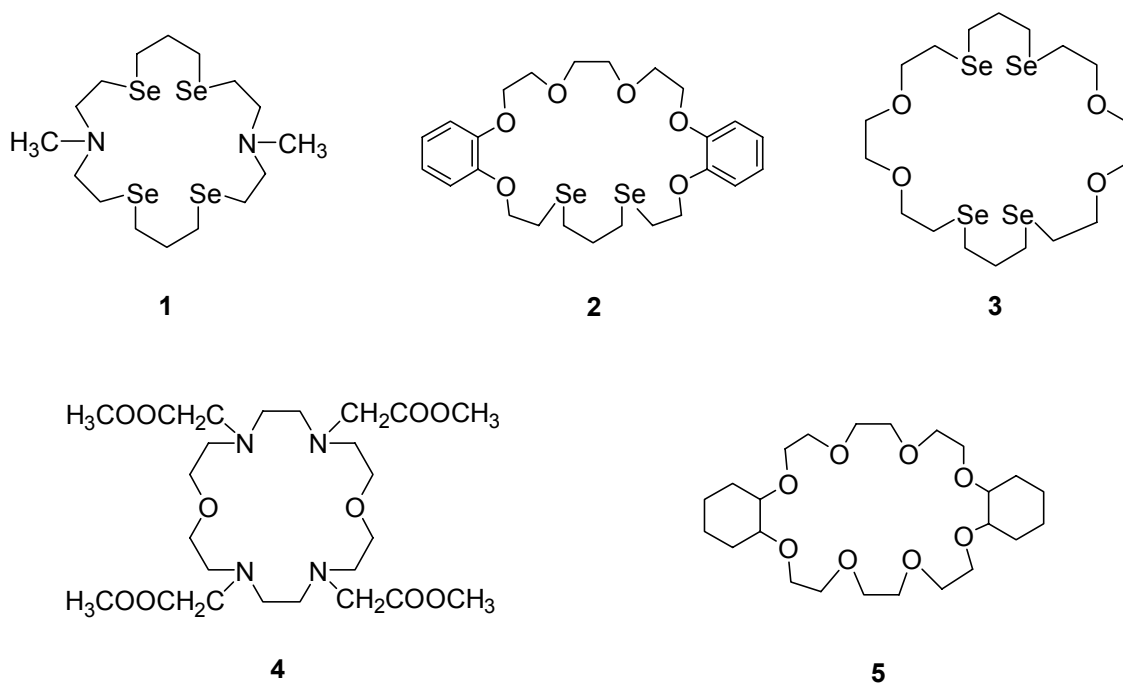
Two new selenacrown ethers, i.e., *N,N'*-dimethyl-1,11-diaza-4,8,14,18,-tetraselenacycloicosane (**1**) and 7,11-diseleno-2,3,15,16,-dibenzo-1,4,14,17,20,23-hexaoxacyclopentacosane (**2**), have been synthesized and characterized by elemental analysis and UV, and <sup>1</sup>H NMR spectroscopy. An X-ray crystallographic structure was obtained for **1**. UV-spectrophotometric titrations have been performed in CCl<sub>4</sub> solution at 25.0–50.0 °C to obtain the complex stability constants (*K<sub>S</sub>*) and the thermodynamic parameters ( $\Delta H^\circ$  and  $T\Delta S^\circ$ ) for the stoichiometric 1:1 complexation of [60]-fullerene (C<sub>60</sub>) with the crown ethers **1-4**. The obtained *K<sub>S</sub>* values together with that reported for dicyclohexano-24-crown-8 (**5**) reveal that, the more the heteroatom numbers in crown ether ring are, and the larger the cavity sizes of crown ethers are, the higher the *K<sub>S</sub>* values for complexation with C<sub>60</sub> are. Thermodynamically, the complexation of C<sub>60</sub> with **1-5** is absolutely enthalpy-driven in CCl<sub>4</sub>, while the complex stability is governed by the entropy term.

## Introduction

Crown ethers are particularly interesting synthetic macrocyclic polyethers due to their ability to form stable inclusion complexes<sup>1</sup> and rotaxanes/pseudorotaxanes<sup>2</sup> with a number of inorganic salts and organic secondary ammonium salts. In particular, chalcogen macrocycles as models for metalloenzymes and metalloproteins in the structure and bonding of metal-chalcogen macrocyclic complexes have attracted intense interest.<sup>3</sup> Furthermore, in the field of systems bearing heavy chalcogens, seleno-ethers exhibiting strongly binding ability with transition metals have been extensively studied too.<sup>4</sup> We have demonstrated recently that selenacrown ethers exhibit very high binding abilities for Ag<sup>+</sup>,<sup>5</sup> and more recently, Kamigata<sup>6</sup> *et al* reported the synthesis and structures of 15- and 18-membered unsaturated selenacrown ethers and their complexation with silver trifluoroacetate. Otherwise, Gleiter<sup>7</sup> *et al* studied self-organization of chalcogen-containing cyclic alkynes and alkenes to yield columnar structures.

On the other hand, crown ether-fullerene conjugates attract substantial interest as advanced supramolecular materials<sup>8</sup> and have found application in sensing devices for cations.<sup>9</sup> There are a number of known instances in which fullerenes have been connected to crown ethers to exploit the well-known complexing properties of these subunits.<sup>10</sup> It is noted that the complexes of fullerenes with the various host molecules have been reported to change fullerene's physical and chemical properties. These investigations are mainly focused on the complexation of cyclodextrins,<sup>11</sup> calixarenes<sup>12</sup> with fullerenes. For example, the water-soluble main-chain polyfullerene reported by Kamigata<sup>13</sup> has a potential application in the biomedical area due to their hydrophilicity. In addition, C60 could be situated inside the cavities constructed by sidearm

of the azacrown ethers and form homogeneous LB mono and multilayers with C60,<sup>14</sup> and dicyclohexano-24-crown-8 and dibenzo-24-crown-8 exhibit a certain extent molecular binding ability for C60.<sup>15</sup> Except for these examples, to the best of our knowledge, the quantitative studies on the complexation of crown ethers with fullerenes were hardly involved. In our present work, we wish to report the syntheses and characterization of two new selenacrown ethers (**1** and **2**) and also their complexation behavior with C60 determined by UV-vis spectrometry. Comparison of the complexation behavior of these selenacrown ethers with that of **3** and **4** as well as that reported for dicyclohexano-24-crown-8 (**5**)<sup>15a</sup> (Chart 1), together with the X-ray crystallographic structure of **1** and the MM2-optimized structures of **3** and **4**, will serve our further understanding of structure –binding ability relationship between fullerenes and crown ethers. It is also interesting to discuss what driven forces are provided for the complexation.



## CHART 1

### Experimental Section

**General.** Melting points, measured with an Xt-4 apparatus, are uncorrected.  $^1\text{H}$  NMR spectra were recorded on a Varian Mercury VX300 instrument in  $\text{CDCl}_3$  solution, using tetramethylsilane as an internal reference. Ultraviolet spectra were recorded on Shimadzu UV-2401/PC instruments fitted with a TB-85 thermo bath (Shimadzu). Elemental analyses were performed on a Perkin-Elmer 2400C instrument.

**Materials.** C60 was commercially available and used as received. The solvent, carbon tetrachloride, was further purified by keeping it in fused calcium chloride for 24h and then distilling just before use. All chemicals were reagent grade and used without further purification unless noted otherwise. The key intermediates 1,2-diselenacyclopentane were prepared according to the literature procedure.<sup>16</sup> The compounds **3** and **4** were synthesized according to the procedures reported previously.<sup>17</sup>

### Synthesis of Selenacrown Ether

***o*-Hydroxy-2-phenyloxy-ethanol (C1).** 8.0 g (0.1 mol) 2-Chlorethanol was added slowly into a solution of 11 g (0.1 mol) catechol and 11.2 g (0.2 mol) potassium hydroxide ground dissolved in 50 mL 2-methoxyethanol under  $\text{N}_2$ , and then the mixture was stirred under 100 °C for 48 h. After cooling, the solvents were removed in *vacuo*, the residue was extracted with  $\text{CHCl}_3$ . Evaporation of the  $\text{CHCl}_3$  gave solid residue, which was purified by column chromatography on silica (200-300 mesh, ethyl acetate) and then recrystallized from methanol to give colorless crystal **C1**

(5.0 g, 36 % yield): mp 99-101°C;  $^1\text{H NMR}$ :  $\delta$  4.14 (m, 4H), 4.90(s, 2H), 6.89 (m, 4H); Anal. Calcd for  $\text{C}_8\text{H}_{10}\text{O}_3$ : C, 62.33; H, 6.54. Found: C, 62.40; H, 5.61.

**1,20-Dihydroxy-4,5,16,17,-dibenzo-3,6,9,12,15,18-hexaoxaheneicosane (C2).** A solution of dissolved 6.0 g (0.013 mol) of triethyleneglycol di(toluenep-sulphonate) in 30 mL THF was added dropwise into a solution of dissolved 4.0 g (0.029 mol) C1 of and 1.2 g (0.3 mol) sodium hydroxide in 35 mL THF. The mixture was stirred under reflux for 24 h, After cooling, the solvents were removed in *vacuo* and the residue was dissolved with ethyl acetate, then was purified by column chromatography on silica (200-300 mesh, ethyl acetate and 4:1 ethyl acetate: ethanol) giving C2 (4.2 g, 77 % yield): mp 77-78 °C;  $^1\text{H NMR}$ :  $\delta$  3.25 (m, 4H), 3.84 (m, 4H), 3.90 (m, 4H), 4.19 (m, 4H), 4.31 (m, 4H), 6.89 (s, 8H); Anal. Calcd for  $\text{C}_{22}\text{H}_{30}\text{O}_8$ : C, 62.55; H, 7.16. Found: C, 62.53; H, 7.18.

**1,20-Di(*p*-toluenesulfonyl)-4,5,16,17,-dibenzo-3,6,9,12,15,18-hexaoxaheneicosane (C3).** The C2 4.22 g(10 mmol) and sodium hydroxide 1.2 g(30 mmol) were added to 20 mL methanol and 20 mL  $\text{H}_2\text{O}$ , and the mixture was stirred in an ice bath, and then added dropwise a solution of 3.4 g *p*-toluenesulfonyl chloride dissolved in 20 mL THF. The resultant mixtures continue stirring for 3 h in an ice bath, then poured into 220 mL ice-water mixture. The precipitate formed was collected by filtration to obtain 6.0 g (yield 82 %) white crystal C3: mp. 88-90°C; UV-vis  $\lambda_{\text{max}}$  ( $\text{CCl}_4$ ) / nm ( $\epsilon / \text{M}^{-1} \text{cm}^{-1}$ ): 273 (5370);  $^1\text{H NMR}$ :  $\delta$  2.42 (s, 6H), 3.73 (s, 4H), 3.84 (m, 4H), 4.19 (m, 4H), 4.31 (m, 4H), 4.34 (m, 4H), 6.84 (m, 4H), 6.91(m, 4H), 7.32(d, 4H), 7.80(d, 4H); Anal. Calcd for  $\text{C}_{36}\text{H}_{42}\text{O}_{12}\text{S}_2$ : C, 59.16; H, 5.79. Found: C, 58.95; H, 5.83.

***N,N'*-Dimethyl-1,11-diaza-4,8,14,18,-tetraselenacycloicosane (1).** 1,2-Diselenacyclopentane

0.2 g (10mmol) was dissolved in absolute ethanol (60 mL) containing sodium hydroxide 0.12 g (30mmol) and sodium borohydride 0.114 g (30mmol) After the ethanol solution became colorless, *N*-methyl-di(chloridethyl)amine in absolute ethanol (10 mL) was added to the solution under a nitrogen atmosphere, and the reaction was carried out under reflux for 6h. After cooling, the solvents were removed in *vacuo*. After the residue obtained was added to a mixture of water (100 mL) and chloroform (60 mL), the resultant binary mixture was stirred vigorously, and the chloroform layer was separated and dried over MgSO<sub>4</sub>. The residue obtained upon evaporation of the chloroform was purified on a silica column chromatogram (dilution 10:1 chloroform/diethyl ether), and then recrystallized from acetone to give colorless crystals of **1** (50 mg, 17 % yield), which are suitable for X-ray crystallography: mp 49-52 °C; UV-vis  $\lambda_{\max}$  (CCl<sub>4</sub>) / nm ( $\epsilon$  / M<sup>-1</sup> cm<sup>-1</sup>): 263.5 (9570); <sup>1</sup>H NMR:  $\delta$  2.72 (m, 24H), 2.39 (s 6H), 2.04 (m, 4H); Anal. Calcd for C<sub>16</sub>H<sub>34</sub>Se<sub>4</sub>N<sub>2</sub>: C, 33.70; H, 6.01; N, 4.91. Found: C, 33.62; H, 6.08; N, 5.28.

**7,11-Diseleno-2,3,15,16,-dibenzo-1,4,14,17,20,23-hexaoxacyclopentacosane (2).** This compound was prepared according to the procedure described above for **1** in 51% yield after recrystallization from hexane: mp 101-103 °C; UV-vis  $\lambda_{\max}$  (CCl<sub>4</sub>) / nm ( $\epsilon$  / M<sup>-1</sup> cm<sup>-1</sup>): 261 (12000); <sup>1</sup>H NMR:  $\delta$  2.10 (m, 2H), 2.91 (m, 8H), 3.82 (m, 4H), 3.91 (m, 4H), 4.16 (m, 4H), 4.27 (m, 4H), 6.89 (s, 8H); Anal. Calcd for C<sub>25</sub>H<sub>34</sub>O<sub>6</sub>Se<sub>2</sub>: C, 51.03; H, 5.82. Found: C, 50.94; H, 5.77.

**X-ray Crystallographic Study.** The X-ray intensity data of **1** were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal-focus molybdenum-target X-ray tube ( $\lambda = 0.71073 \text{ \AA}$ ) operated at 2.0 kW (50 kV, 40 mA) and a graphite monochromator.  $T = 293 \text{ K}$ . Crystallographic data for Compounds **1** are summarized in Table 1. The structure was

solved by using direct method and refined employing full-matrix least squares on  $F^2$  (Siemens, SHELXTL, version 5.04).

**TABLE 1.** Crystal Data and Data Collection Parameters for **1**.

Data	<b>1</b>
Empirical formula	C16 H38 N2 O2 Se4
Formula weight	606.32
$T$ (K)	293(2) K
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	$a = 22.038(6) \text{ \AA}$ , $\alpha = 90^\circ$ . $b = 5.2657(14) \text{ \AA}$ , $\beta = 113.443(4)^\circ$ $c = 22.387(6) \text{ \AA}$ , $\gamma = 90^\circ$ .
$V \text{ \AA}^3$	2383.5(11)
$Z$	4
$D_C \text{ mg/m}^3$	1.690
$F(000)$	1200
Crystal size	0.30 × 0.25 × 0.20 mm
Theta range for data collection	1.98 to 25.02°.
Data / restraints / parameters	2104 / 0 / 119
Reflections collected / unique	3990 / 2104 [R(int) = 0.0481]
Goodness-of-fit on $F^2$	0.993
$R$ (wR2) [ $I > 2\sigma(I)$ ]	0.0469 (0.1012)
$R$ (wR2) (all data)	0.1109 (0.1215)
Largest diff. peak and hole e. $\text{\AA}^{-3}$	0.491, -0.392

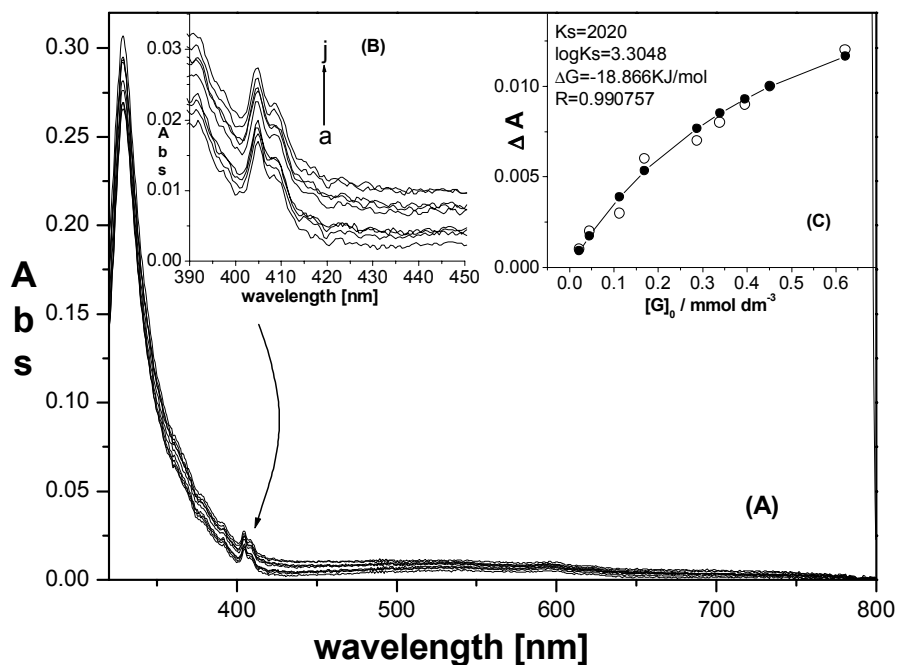
## Results and Discussion

**Synthesis.** Selenacrown ethers **1** and **2** were synthesized in stepwise manners, as shown in

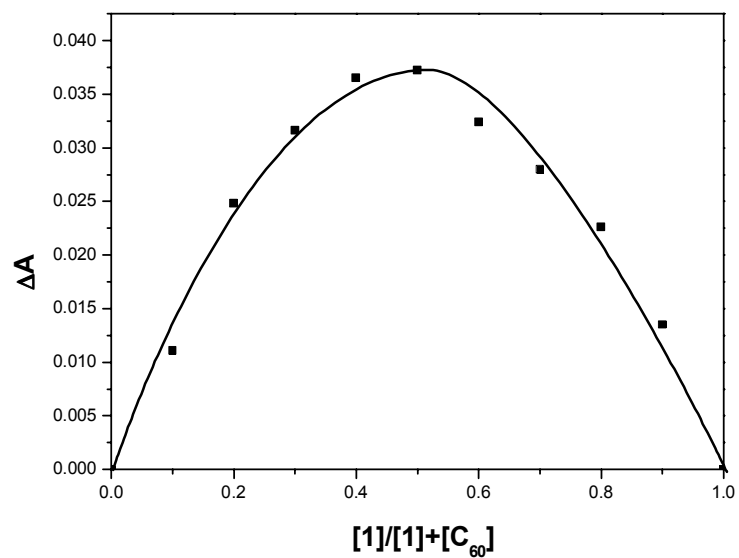
Scheme 1. However, the intermediate sodium 1,3-propanediselenolate actually was not further purified, so or rather, the preparation of **1** belongs to one step reaction. One may note that the yield of **2** (51 %) is higher than that of **1** (17 %), which might be attributed to two factors. 1) Crown ether **1** is the product of 2+2 cyclization reaction, while crown ether **2** is that of 1+1 cyclization reaction. It is known that synthesizing cyclocompound demands the two ends of open link chain compounds to be near enough to bond, and therefore, the 2+2 cyclization reaction would obtain more by-product than the 1+1 cyclization reaction, corresponding lower yield for the former. 2) The templet effect of Na<sup>+</sup> is an important for improving compound yields. In the light of the Hard-Soft Acid-Base theory, the interaction of soft selenium donor with hard Na<sup>+</sup> cation is weaker than that of hard oxygen donor with hard Na<sup>+</sup> cation. Consequently, NaOH in the reaction system for preparing **1** provides only basic environment, while NaOH for preparation of **2** not only offers basic environment, but also can be used as a template because of coordination between oxygen atoms in **C3** and Na<sup>+</sup> cation.



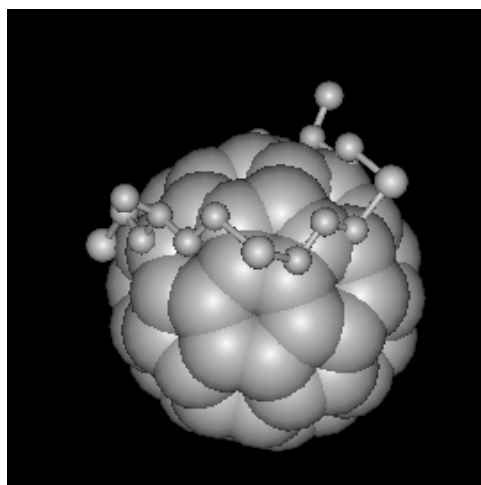
the continuous variation method. Figure 2 illustrates the continuous variation plot for **1**/C60 system. In the concentration range, the plot for crown ether **1** shows a maximum at a molar fraction of 0.5, indicating 1:1 inclusion complexation. Based on the size of crown ether **1** vs the size of the fullerene, we did a molecular modeling of the inclusion complexation upon **1** with C60 using the CS Chem 3D 8.0 and Web Labviewer 3.7 software (Figure 3), and the result obtained also support the 1:1 stoichiometry.



**FIGURE 1.** (A) UV-vis spectral changes of  $\text{CCl}_4$  solution of C60 ( $4.17 \mu\text{M}$ ) in the presence of compound **1**. The concentration of **1** (from a to j): 0, 22.6, 45.2, 113, 169.5, 287.5, 339, 395.5, 452, 621.5  $\mu\text{M}$ , respectively. (B) Insert 390-450 nm range expanded for clarity. (C) Least-squares curve-fitting analyses for complexations of C60 with **1**.

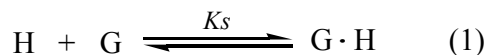


**FIGURE 2.** Continuous variation plot of **1** /C<sub>60</sub> in CCl<sub>4</sub> at 25°C ([**1**] + [C<sub>60</sub>] = 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>)



**FIGURE 3.** Molecular modeling of the inclusion complexation upon **1** with C<sub>60</sub> using the CS Chem 3D 8.0 and Web Labviewer 3.7 software.

For stoichiometric 1:1 complexation, the complexation of guest (G) with host (H) is expressed by Equation (1):



The UV spectral changes ( $\Delta A$ ) upon addition of crown ethers are proportional to the concentration of complex formed and the difference of molar extinction coefficients between free host and complexed one may be taken as the proportionality coefficient, *i.e.*  $\Delta A = \Delta \epsilon [\text{H} \cdot \text{G}]$ . Thus, the complex stability constant ( $K_s$ ) should be defined by using eqn. (2)<sup>18</sup>.

$$K_s = \frac{[\text{H} \cdot \text{G}]}{[\text{H}][\text{G}]} = \frac{[\text{H} \cdot \text{G}]}{([\text{G}]_0 - [\text{H} \cdot \text{G}])([\text{H}]_0 - [\text{H} \cdot \text{G}])} = \frac{\Delta A / \Delta \epsilon}{([\text{G}]_0 - \Delta A / \Delta \epsilon)([\text{H}]_0 - \Delta A / \Delta \epsilon)} \quad (2)$$

After some manipulation, equation (2) yields (3)

$$\Delta A = \{\Delta \epsilon([\text{H}]_0 + [\text{G}]_0 + 1 / K_s)\} \pm \sqrt{\Delta \epsilon^2([\text{H}]_0 + [\text{G}]_0 + 1 / K_s)^2 - 4\Delta \epsilon^2[\text{H}]_0[\text{G}]_0} / 2 \quad (3)$$

The complex stability constant ( $K_s$ ) can be calculated from the analysis of the sequential changes in absorption intensity ( $\Delta A$ ) at varying host concentrations by using a nonlinear least-squares method according to the curve fitting Equation (3):

Here  $[\text{G}]_0$  and  $[\text{H}]_0$  refer to the initial concentrations of C60 and crown ether, respectively, and  $\Delta \epsilon$  is the proportionality coefficient, which may be taken as a sensitivity factor for the absorption change and is a quantitative measure of conformational change upon complexation with guest.<sup>19</sup> For hosts **1-4** examined, the  $\Delta A$  values were plotted as a function of  $[\text{G}]_0$  to give excellent fits; this validated the 1:1 stoichiometry assumed above. In repeated measurements, the  $K_s$  values were reproducible within an error of  $\pm 5\%$ . The experiments were repeatedly performed at 25.0, 30.0, 35.0, 40.0, 45.0 and 50.0 °C, and the  $K_s$  values, Gibbs free energy changes ( $-\Delta G^\circ$ ) and  $\epsilon$  values obtained by the curve fitting<sup>20</sup> were listed in Table 2. The results indicate that the stability constants ( $K_s$ ) and Gibbs free energy changes ( $-\Delta G^\circ$ ) were decreased with increases in

temperature. However, sensitivity factor  $\Delta\epsilon$  didn't showed direct correlation with the complex stability, and the most stable complex didn't afford the most drastic absorption change and vice versa. Absorption change  $\Delta\epsilon$  value of crown ether **1** with C60 was increased with increased in temperature, while absorption changes  $\Delta\epsilon$  of other crown ethers were first increased and then decreased with increased in temperature.

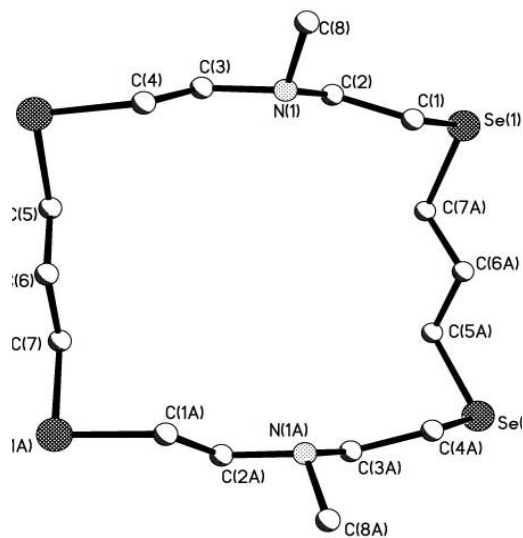
**TABLE 2.** Stability Constants ( $\ln K_s$ ) and Gibbs Free Energy Changes ( $-\Delta G^\circ$ ) for the Complexation of the Crown Ethers with C60 at 298-323 K in  $\text{CCl}_4$

Host	Temp. / K	$K_s / \text{M}^{-1}$	$\Delta\epsilon$	$\ln K_s$	$-\Delta G^\circ / \text{KJ.mol}^{-1}$
<b>1</b>	298	2020	4740	7.61	18.9
	303	1020	4870	6.93	17.5
	308	759	6460	6.63	17.0
	313	443	10010	6.09	15.8
	318	298	53390	5.70	15.1
<b>2</b>	298	1450	980	7.28	18.0
	303	742	4710	6.61	16.7
	308	449	6780	6.11	15.6
	313	278	16910	5.63	14.7
	318	130	6640	4.87	12.9
	323	80	36590	4.38	11.8
<b>3</b>	298	1512	1740	7.32	18.1
	303	925	1900	6.83	17.2
	308	813	2660	6.70	17.2
	318	587	2040	6.38	16.9
	323	498	2390	6.21	16.7
<b>4</b>	298	1400	5230	7.24	17.9
	303	1073	6540	6.98	17.6
	308	868	83770	6.77	17.3
	318	642	10790	6.46	17.1
	323	470	4640	6.15	16.5
<b>5<sup>a</sup></b>	288	1109		7.01	16.8
	296	752		6.62	16.3
	304	490		6.19	15.6

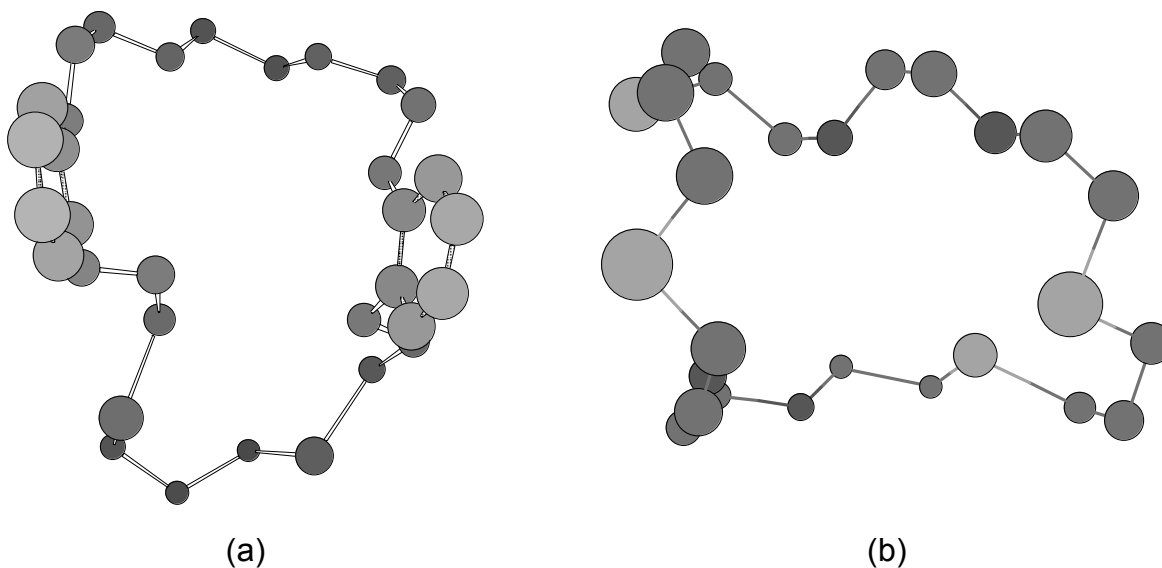
312	381	5.94	15.4
319	268	5.59	14.8

<sup>a</sup> reference [15a].

**Molecular Binding Ability.** As can be seen from Table 2, the complexation of **1** with C60 exhibit the highest  $K_s$  value up to  $2020 \text{ M}^{-1}$ , those of **2-4** do the moderate  $K_s$  values at 298 K, and that of **5** does the lowest  $K_s$  value. C60 is considered to have similar properties to transition metals and octahedral coordination sites from Yoshida's "superatom concept",<sup>21</sup> and it has been also demonstrated that seleno-<sup>4</sup> or aza-crown ethers<sup>22</sup> showed stronger complexation with transition metals than the crown ethers bearing oxygen. Therefore, it is reasonable that the  $K_s$  values for complexation of **1-4** with C60 are higher than that of **5** with C60. On the other hand, it is interesting to note that selenacrown ethers **1** and **3** contain the same selenium atoms, but shows different complexation ability with C60, which may be attributed to their different cavity sizes. Judging from the results of the crystal structure of compound **1** (Figure 4), the diagonal Se-Se distances of **1** are 10.1 Å and 9.7 Å, respectively. Taking the van der Waals radius of the selenium atom (2.3 Å) into consideration, the cavity size of **1** is estimated at 7.8 Å × 7.4 Å. The cavity size of **3** obtained from its the MM2-optimized structure (Figure 5b) is estimated at 7.2 Å × 7.3 Å (the diagonal Se-Se). Therefore, crown ether **1** is more advantageous to complexation with C60 than that of crown ether **3**, leading to the higher  $K_s$  value. Upon complexation with C60, **2** affords less selenium atoms than **3**, which is however compensated by its larger cavity size (7.8 Å × 7.6 Å, Figure 5a), resulting in approximate  $K_s$  values.



**FIGURE 4.** X-ray structure of seleno-azacrown ether **1**, H<sub>2</sub>O was omitted for clarity.



**FIGURE 5.** MM2-optimized structures of (a) **2**, and (b) **3**.

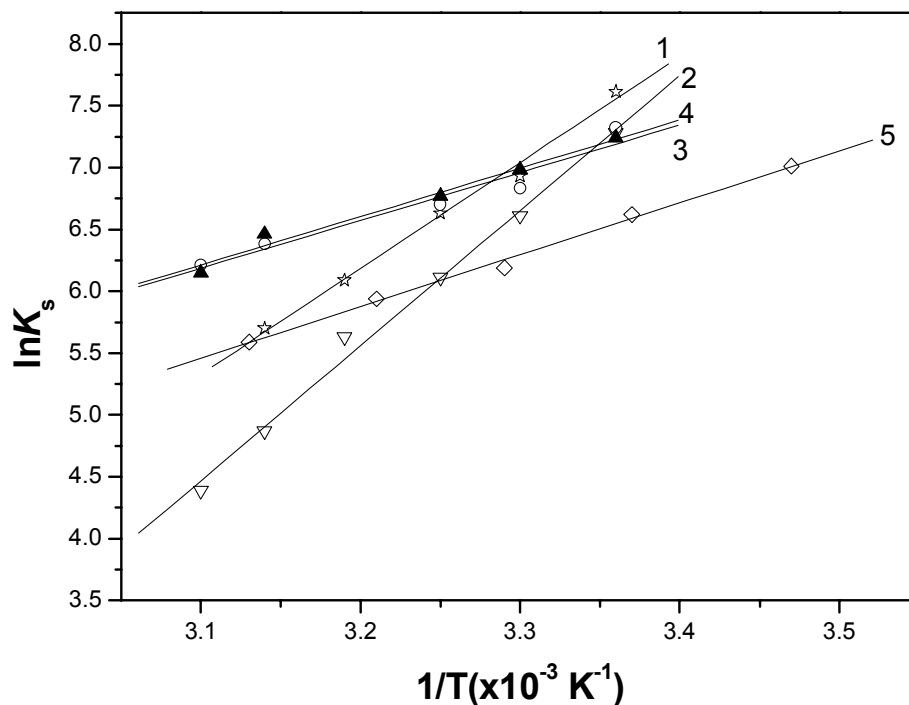
**Thermodynamic Parameter.** The free energy changes ( $\Delta G^\circ$ ) for complexation of the crown ether with C<sub>60</sub> are calculated from the equilibrium constant  $K_s$  by Equation (3) and is related to the enthalpic and entropic changes ( $\Delta H^\circ$  and  $\Delta S^\circ$ ) through the Gibbs–Helmholtz Equation (4):

$$\Delta G^\circ = -RT \ln K_S \quad (3)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

$$\ln K_S = -\Delta H^\circ / RT + \Delta S^\circ / R \quad (5)$$

Combining Equations (3) and (4), we obtain Equation (5), which describes the temperature dependence of  $K_S$ . Thus, the  $\ln K_S$  values, shown in Table 2, are plotted as a function of the inverse temperature to give good linear relationships. The Van't Hoff plot for the complexation of C60 with crown ethers is shown in Figure 6. The thermodynamic parameters of crown ethers 1-4 obtained are listed in Table 3. For comparison purpose, the thermodynamic parameters reported for the complexation with crown ether 5 are also included in Table 3.



**FIGURE 6.** Van't Hoff plots of  $\ln K_S$  versus  $1/T$  in spectrophotometric titrations of **1** (☆), **2** (▽), **3** (○), **4** (▲), and **5** (◇) with C60.

**TABLE 3.** Thermodynamic Parameters ( $\text{kJ}\cdot\text{mol}^{-1}$ ) for 1:1 Complexation of C60 with Crown Ethers **1-5** at 25 °C in  $\text{CCl}_4$ .

Crown ether	$-\Delta G^\circ$	$-\Delta H^\circ$	$T\Delta S^\circ$
<b>1</b>	18.9	70.6	-51.7
<b>2</b>	18.0	90.7	-72.7
<b>3</b>	18.1	32.1	-14.0
<b>4</b>	17.9	32.5	-14.6
<b>5</b> <sup>a</sup>	16.1	33.9	-17.8

<sup>a</sup> reference [15a].

As can be readily recognized from Table 3, all the enthalpy changes ( $\Delta H^\circ$ ) and entropy changes ( $T\Delta S^\circ$ ) for the complex formation of crown ethers with C60 are negative, indicating that these reactions are chiefly enthalpy-driven in  $\text{CCl}_4$ . The larger enthalpic gains ( $-\Delta H^\circ$ ) for **1** and **2** than for **3**, **4** and **5** may suggest stronger the interactions of rich-electron atoms with double bond carbons of C60<sup>21</sup> and/or  $\pi$ - $\pi$  interactions between the C60 and the donors **1** and **2**, but the large enthalpic gains do not immediately mean high complex stability and is often canceled out by the larger entropic loss arising from structural freezing upon complexation. As compared with **2**, conformational flexibility of **1** inevitably decrease the entropic loss for C60 by  $21.0 \text{ kJ}\cdot\text{mol}^{-1}$ , leading to high complex stabilities.

It is interesting to compare the thermodynamic parameters for the complexation of a series of crown ethers **2**, **3** and **5** with C60. As can be seen from Table 3, the enthalpy changes for **2** are much greater than for **3** and **5**, indicating that introduction of aromatic groups into the crown ether ring results in  $\pi$ - $\pi$  interactions between **2** and C60. The entropy changes for the

complexation of **2**, **3** and **5** decrease in the following order:  $2 > 5 > 3$ . Close examination of the MM2 molecular structure of free **2** reveals that the two aromatic rings skeleton in **2** is almost parallelly situated in the same side of crown ether ring. Upon complexation of C60, the two aromatic rings in **2** would change the original conformation, making the molecule of **2** suffer more extensive structural freezing, and leading to more unfavorable entropy change than **3** and **5**. It is concluded that the complexation of C60 with **1-5** is obviously enthalpy-driven in CCl<sub>4</sub>, but the complex stability is governed by the entropy term.

## Conclusion

In summary, two new selenacrown ethers (**1** and **2**) were synthesized in distinct yields. The complex stability constants and the thermodynamic parameters for complexation of C60 with the crown ethers **1-4** were determined by UV-spectrophotometric titrations, showing the highest *K<sub>s</sub>* value for **1**. Furthermore, the factors affecting molecular binding ability were discussed from the electron effect and size/shape-fit concept, revealing that the heteroatom numbers and the cavity sizes are key factors to stability constant values. Thermodynamically, the complexation of C60 with **1-5** is absolutely enthalpy-driven, while the complex stability is governed by the entropy term. The present investigations would be useful not only for designing novel supramolecular host compounds for optimizing complexation with fullerenes, but also for controlling the complexation phenomena of crown ethers.

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**Supporting Information Available:** The CIF file of crystal **1** is showed in Supporting Information.

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## Graphical Abstract

### Synthesis of Some Selenacrown Ethers and the Thermodynamic Origin of Their Complexation with C60

Yu Liu,<sup>\*</sup> Jian-Rong Han, Yan-Li Zhao, Heng-Yi Zhang, and Zhong-Yu Duan

