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# Synthesis and Structures of 15- and 18-Membered Unsaturated Selenacrown Ethers and Their Complexation with Silver Trifluoroacetate

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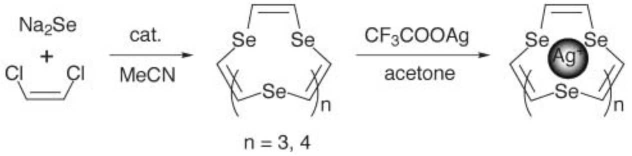
## ABSTRACT



**The reaction of Na$_2$Se with *cis*-dichloroethene yielded (*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13-pentaselenacyclopentadeca-2,5,8,11,14-pentaene (15-US-5) and (*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16-hexaselenacyclooctadeca-2,5,8,11,14,17-hexaene (18-US-6). X-ray crystallographic analysis of 15-US-5 and 18-US-6 revealed an all-*cis* geometry around the carbon–carbon double bonds, with all of the selenium atoms located on one side of the respective ring planes. 15-US-5 and 18-US-6 were also found to be oxidized more easily than the corresponding sulfur analogues. The complexation of 15-US-5 and 18-US-6 with silver trifluoroacetate afforded Ag$^{\mathrm{I}}$(15-US-5)(CF$_3$COO) and Ag$^{\mathrm{I}}_5$(18-US-6)$_3$(CF$_3$COO)$_5$, respectively.**

Recently, much attention has been focused on the chemistry of heavier crown ethers.[1] In particular, transition metal inclusion behavior of the thiacrown ethers is of interest in relation to crown ethers.[1−3] 18-Membered thiacrown ether is known to react with 1, 2, and 3 equiv of silver ion to give 1:1, 1:2, and 1:3 complexes, respectively, and it has been shown to have no selectivity for the metal inclusion number, probably because of the high flexibility of the ring system.[4] We have synthesized conformationally restricted unsaturated thiacrown ethers with all-*cis* geometry around the carbon−carbon double bonds, examined their inclusion behavior, and found that they exhibited selectivity for the number of metals included in their cavities.[5,6] After our report concerning unsaturated thiacrown ethers in 2001,[5] Gleiter and co-workers instantly reported in 2002 the synthesis of thiacrown ethers possessing both saturated and unsaturated carbon−carbon bonds,[7] indicating that crown ethers with carbon−carbon unsaturated bonds are given attention. On the other hand, some selenacrown ethers (selenium coronands) have also been synthesized,[8−10] and their structures[8,11] and complexa-

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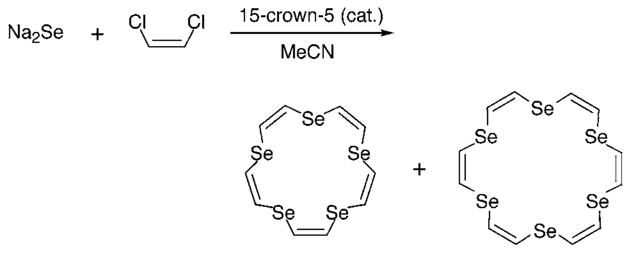
tions[10,12,13] with transition metals have been studied over the past 15 years. To our knowledge, however, there is no report concerning their unsaturated systems with carbon−carbon double bonds. In this study, we synthesized unsaturated selenacrown ethers by reacting sodium selenide with *cis*-dichloroethene. We report herein the synthesis and structures of 15- and 18-membered unsaturated selenacrown ethers and their complexation with silver trifluoroacetate.

When an acetonitrile solution containing excess *cis*-dichloroethene was added to sodium selenide, prepared from selenium, sodium hydroxide, and Rongalit in water,[14] in the presence of a catalytic amount of 15-crown-5, several unsaturated selenacrown ethers were formed (total 16%) after 60 h of stirring. Among the products, 15- and 18-membered unsaturated selenacrown ethers (15-US-5 and 18-US-6)[15] **1** and **2** were isolated as crystals in 12% and 27% toward the total macrocycles, respectively, by silica gel column chromatography (hexane/acetone = 2/1), followed by gel permeation chromatography (chloroform). In this reaction, 15-crown-5 was an indispensable catalyst; without 15-crown-5, compound **1** was not produced and **2** was formed in trace amounts.



15-US-5 (**1**) 18-US-6 (**2**)

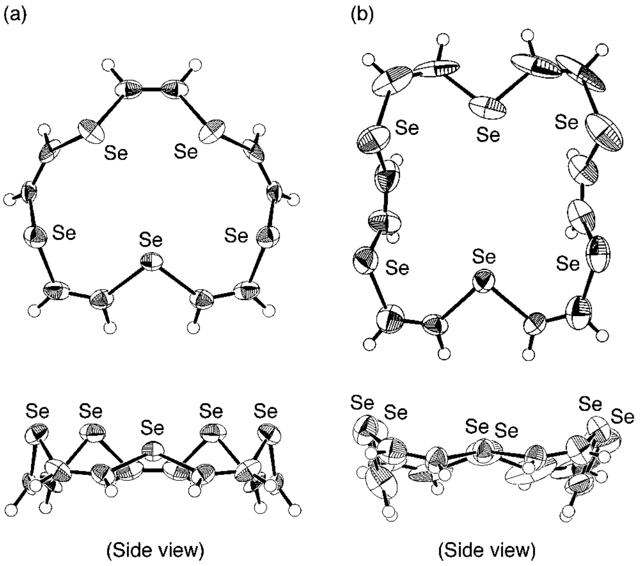


**Figure 1.** ORTEP drawings of (a) 15-U-5 (**1**) and (b) 18-US-6 (**2**) showing thermal ellipsoids at 50% probability level.

The crystal structures of **1** and **2** were determined by X-ray crystallographic analysis, as shown in Figure 1.[16] All carbon−carbon double bonds of the two compounds exhibit *cis* geometry, and the bond lengths, angles, and dihedral angles are almost normal for both of the crystal structures. All selenium atoms of both compounds are located on one side of the respective ring planes, whereas sulfur atoms of the corresponding 15-membered unsaturated thiacrown ether (15-UT-5) are located on both sides of the ring.[5] The most interesting feature of the structures of **1** and **2** is hole size of the molecules. The distance between the center of all of the selenium atoms and the selenium atoms is 2.77 Å (average) in the crystalline state for **1**, which is almost the same as that for the corresponding sulfur analogue 15-UT-5 (2.73 Å). However, the distance for **2** is 3.31 Å, which is longer than that for corresponding sulfur analogue 18-UT-6 (3.01 Å), indicating that compound **2** has a larger cavity in the molecule than its sulfur analogue.

$^1$H and $^{13}$C NMR spectra of **1** and **2** showed only one signal each, indicating that the compounds still have flex-

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(15) In this paper, unsaturated selenacrown ethers are abbreviated as x-US-y (US, *u*nsaturated *s*elenacrown ether; x, *x*-membered ring; y, number of selenium atom).

(16) Crystal structure analysis for **1**: formula $C_{10}H_{10}Se_5$, $M_r = 524.99$, crystal dimensions 0.40 × 0.40 × 0.03 mm$^3$, $a = 8.746(2)$, $b = 18.482(4)$, $c = 8.728(3)$ Å, $V = 1410(1)$ Å$^3$, $\rho_{calcd} = 2.471$ g cm$^{-3}$, $Z = 4$, orthorhombic, space group *Pnma* (No. 62), Rigaku AFC7R diffractometer, $\lambda = 0.71069$ Å, $T = 173$ K, 1889 measured reflections, 1666 unique, $R1 = 0.069$. Crystal structure analysis for **2**: formula $C_{12}H_{12}Se_6$, $M_r = 629.99$, crystal dimensions 0.40 × 0.40 × 0.25 mm$^3$, $a = 15.928(4)$, $b = 19.985(4)$, $c = 10.844(4)$ Å, $V = 3451(1)$ Å$^3$, $\rho_{calcd} = 2.424$ g cm$^{-3}$, $Z = 8$, orthorhombic, space group *Pbca* (No. 61), Rigaku AFC7R diffractometer, $\lambda = 0.71069$ Å, $T = 243$ K, 4018 measured reflections, 3575 unique, $R1 = 0.051$.

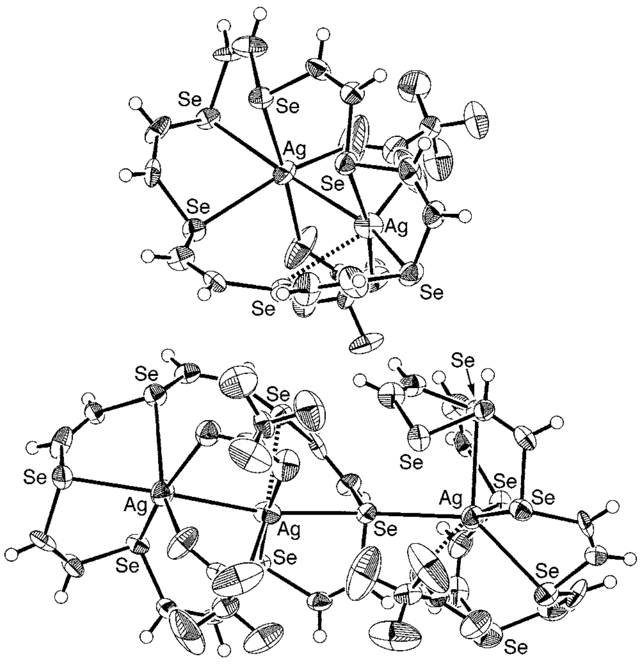

**Figure 2.** ORTEP drawing of $Ag^I_5(18\text{-US-}6)_3(CF_3COO)_5$ (**4**) showing thermal ellipsoids at 50% probability level.

ibility to a certain extent in solution. The chemical shifts of **1** and **2** on the $^1H$ NMR spectra are 7.16 and 7.12 ppm in $CDCl_3$, and those on the $^{13}C$ NMR spectra are 127.0 and 125.7 ppm, respectively. The chemical shifts of **1** and **2** on the $^1H$ NMR spectra are found at lower fields than those of the corresponding sulfur analogues 15-UT-5 and 18-UT-6 (6.48 and 6.40 ppm, respectively),[5] while the chemical shifts on the $^{13}C$ NMR spectra are almost same as those of the corresponding sulfur analogues. Theoretical calculations for the geometries of the unsaturated thia- and selenacrown ethers, obtained from X-ray crystallographic analysis, revealed that the hydrogens of **1** and **2** are slightly more electropositive than those of 15-UT-5 and 18-UT-6 and that the selenium atoms are also slightly more electropositive than the sulfur atoms, whereas the carbon atoms of **1** and **2** are more electronegative than those of the corresponding sulfur analogues.[17]

The cyclic voltammograms of **1** and **2**, measured in acetonitrile using a platinum working electrode, showed irreversible oxidation peaks at +0.75 and +0.74 V, respectively, versus $Fc/Fc^+$, with a scanning potential range of +2.0 to −2.0 V. These values are smaller than those of the corresponding unsaturated thiacrown ethers. This result indicates that the unsaturated selenacrown ethers are oxidized more easily than the corresponding unsaturated thiacrown ethers. The UV spectra of **1** and **2** in various solvents showed $\lambda_{max}$ corresponding to $n \rightarrow \pi^*$ at 252−271 nm.

The reaction of **1** with equimolar silver trifluoroacetate in acetone afforded silver(I) complex, $Ag^I(15\text{-US-}5)(CF_3COO)$ (**3**), as colorless prisms in 66% yield after crystallization by partial evaporation of the solvent. The reaction with 2 equiv of silver trifluoroacetate, however, did not give a stable complex. On the other hand, the reaction of **2** with 2 equiv of silver trifluoroacetate yielded $Ag^I_5(18\text{-US-}6)_3(CF_3COO)_5$ (**4**) as yellow crystals in 61% yield, whereas no stable silver complex was obtained by the reaction with equimolar silver trifluoroacetate. The crystal structure of **4** was determined by X-ray crystallographic analysis. In the crystalline state, one 18-US-6 includes one silver atom and the other two macrocycles include two silver atoms, respectively, as shown in Figure 2.[18] In the case of corresponding unsaturated thiacrown ether (18-UT-6), 1:1 complex, $Ag^I(18\text{-UT-}6)(CF_3COO)$, has been obtained as stable crystals.[6] This difference of the complexation is considered to depend on the cavity size of the macrocycles. In solution, $^1H$ NMR spectrum of **4** showed only one singlet signal. This result indicates that there is facile interconversion between $Ag^I(18\text{-US-}6)(CF_3COO)$ and $Ag^I_2(18\text{-US-}6)(CF_3COO)_2$ in solution.

$$\mathbf{1} + CF_3COOAg \xrightarrow[\text{acetone}]{} \underset{\mathbf{3}}{Ag^I(15\text{-US-}5)(CF_3COO)}$$

$$\mathbf{2} + 2\ CF_3COOAg \xrightarrow[\text{acetone}]{} \underset{\mathbf{4}}{Ag^I_5(18\text{-US-}6)_3(CF_3COO)_5}$$

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**Supporting Information Available:** Detailed information of the X-ray crystallographic analysis of **1**, **2**, and **4**, including structure diagram, details of data collection and reduction and structure solution and refinement, tables of positional and thermal parameters, and bond lengths, angles, and torsional angles. Spectral data including $^1H$, $^{13}C$, and $^{77}Se$ NMR, IR, UV, mass spectra, and elemental analysis of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Atomic charges for crystal structures of **1**, **2**, and corresponding sulfur analogues (15-UT-5 and 18-UT-6) were calculated by using B3LYP with the LANL2DZ basis set. The calculated atomic charges (averages) are as follows. For **1**: C, −0.439; H, 0.301; Se, 0.277. For **2**: C, −0.450; H, 0.305; Se, 0.290. For 15-UT-5: C, −0.393; H, 0.259; S, 0.269. For 18-UT-6: C, −0.429; H, 0.301; S, 0.257.

(18) Crystal structure analysis for **4**: formula $C_{46}H_{36}Ag_5F_{15}O_{10}Se_{18}$, $Mr = 2994.38$, crystal dimensions 0.70 × 0.60 × 0.60 mm$^3$, $a = 11.375(3)$, $b = 18.596(10)$, $c = 20.07(1)$ Å, $\alpha = 63.17(2)$, $\beta = 74.83(2)$, $\gamma = 75.42(2)°$, $V = 3611(2)$ Å$^3$, $\rho_{calcd} = 2.753$ g cm$^{-3}$, $Z = 2$, triclinic, space group $P$1bar (No. 2), Rigaku RAXIS−RAPID Imaging Plate, $\lambda = 0.71069$ Å, $T = 173$ K, 32862 measured reflections, 15700 unique, $R1 = 0.086$.