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Silver Complexes with Unsaturated Thiacrown Ethers: Inclusion Behavior of Conformationally Restricted Macrocycles

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The reactions of 18- and 21-membered unsaturated thiacrown ethers, 18-UT-6 and 21-UT-7, with CF_3COOAg in acetone afforded novel silver(I) complexes Ag^{I}(18-UT-6)(CF_3COO) and Ag^{I}_2(21-UT-7)(CF_3COO)$_2$, respectively. The crystal structure of Ag^{I}(18-UT-6)(CF_3COO) shows that the silver atom occupies the cavity of the 18-UT-6 and the geometry around the silver atom has a distorted five-coordinate square pyramidal arrangement. The crystal structure of Ag^{I}_2(21-UT-7)(CF_3COO)$_2$ shows that the two silver atoms and all sulfur atoms are nearly coplanar and the two trifluoroacetate groups are located at the opposite sides of the plane. The stoichiometry for the complexation of 15-UT-5, 18-UT-6, and 21-UT-7 with CF_3COOAg in solution was examined by ^{1}H NMR measurement. The titration plots of 15-UT-5 and 21-UT-7 show a distinct inflection point at 1:1 and 2:1 metal/macrocycle ratios, respectively, whereas the plot of 18-UT-6 gradually changes at the range of 1:1 to 2:1. From these results, 15-UT-5 and 21-UT-7 were found to show inclusion selectivity for number of silver ions, respectively, whereas 18-UT-6 showed low selectivity for the inclusion number of metals. Comparison of the oxidation and reduction potentials of the silver(I) complexes with those of free macrocycles and CF_3COOAg revealed that unsaturated thiacrown ethers become difficult to be oxidized by complexation with CF_3COOAg, and CF_3COOAg becomes difficult to be reduced by complexation with unsaturated thiacrown ethers.

Introduction

The development of thiacrown ether chemistry over the past 20 years has furnished information concerning their syntheses, structures, and coordination properties.[1,2] In particular, regarding the coordination properties, it is known that thiacrown ethers coordinate to transition metals[1,3] whereas their corresponding oxygen analogues, crown ethers, prefer to coordinate to alkaline and alkaline earth metals.[4] Sevdić,[5] Sekido,[6] and their co-workers have reported that reactions of a saturated thiacrown ether, 1,4,7,10,13,16-hexathiacyclooctadecane (18S6), with 1, 2, and 3 equiv of silver(I) picrate or silver(I) perchlorate afforded 1:1, 2:1, and 3:1 metal/macrocycle complexes, respectively. This phenomenon of forming complexes with various metal/macrocycle ratios may be due to the flexible structure of 18S6. On the other hand, unsaturated thiacrown ethers with *cis*-geometry of the carbon−carbon double bonds are considered to be more conformationally restricted than the corresponding saturated compounds. Therefore, high selectivity for the inclusion number of metals is expected in the complexation of the unsaturated thiacrown ethers with transition metals. Recently, we reported the synthesis of novel unsaturated thiacrown ethers and the complexation of 15-membered unsatur-

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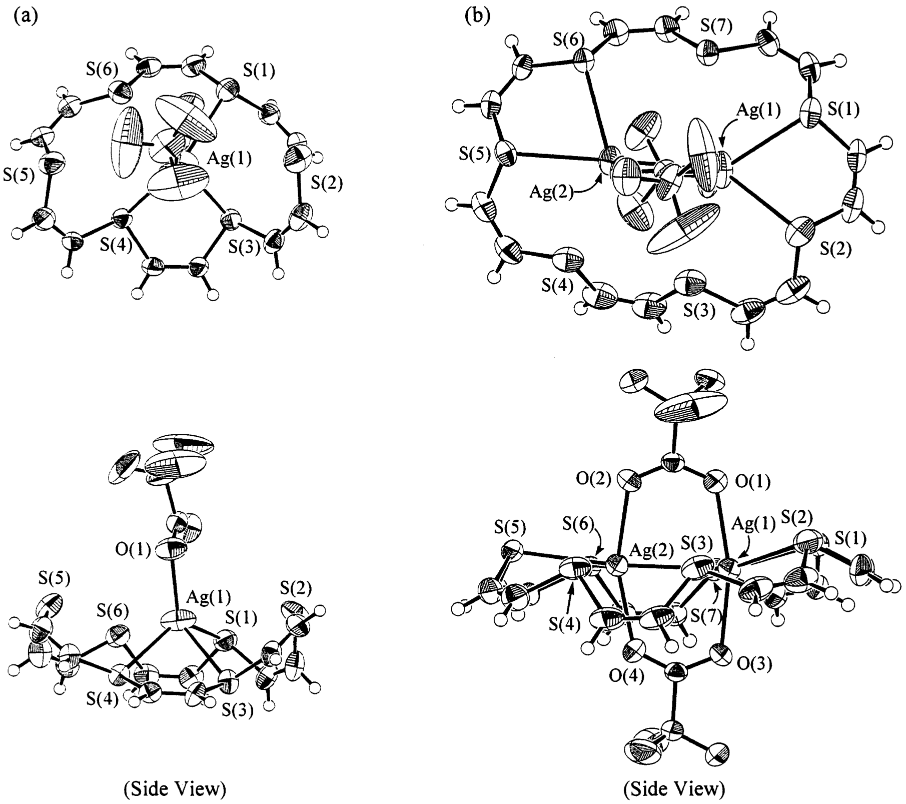
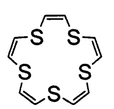
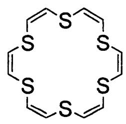


FIGURE 1. ORTEP drawings of (a) $Ag^I(18\text{-UT-6})(CF_3COO)$ (**5**) and (b) $Ag^I_2(21\text{-UT-7})(CF_3COO)_2$ (**6**) showing thermal ellipsoids at 50% probability level.

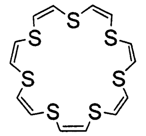
ated thiacrown ether 15-UT-5 (**1**) with equimolar CF_3COOAg to form the 1:1 complex, $Ag^I(15\text{-UT-5})(CF_3COO)$ (**2**).[7] The crystal structure of **2** showed that the silver atom was included in the cavity of **1**. In this paper, we report the synthesis, crystal structures, and redox properties of silver(I) complexes with 18- and 21-membered unsaturated thiacrown ethers 18-UT-6 (**3**) and 21-UT-7 (**4**). Selectivity for the inclusion number of metals in solution was also examined on the basis of titration plots of **1**, **3**, and **4** with CF_3COOAg by ^1H NMR measurement.



1: 15-UT-5



3: 18-UT-6



4: 21-UT-7

Results and Discussion

Synthesis. The reaction of **3** with equimolar CF_3COOAg in acetone afforded a silver(I) complex, $Ag^I(18\text{-UT-6})(CF_3COO)$ (**5**), as colorless prisms in 63% yield. The ratio of CF_3COOAg to **3** in the complex was determined by elemental analysis. The silver(I) complex **5** was stable in air in the crystalline state and also stable in acetone solution even after 1 month. Similarly, the reaction of **4** with equimolar CF_3COOAg was carried out; however, no stable silver(I) complex was obtained. This result indicates that the cavity size of **4** may be too large for one silver ion. Therefore, the reaction of **4** with 2 equiv of CF_3COOAg was examined. In this case, a 2:1 silver(I) complex, $Ag^I_2(21\text{-UT-7})(CF_3COO)_2$ (**6**), was obtained as stable colorless prisms in 85% yield:

$$\mathbf{3} + CF_3COOAg \xrightarrow[\text{acetone}]{\text{rt}} Ag^I(18\text{-UT-6})\,(CF_3COO) \quad \mathbf{5}$$

$$\mathbf{4} + 2CF_3COOAg \xrightarrow[\text{acetone}]{\text{rt}} Ag^I{}_2(21\text{-UT-7})\,(CF_3COO)_2 \quad \mathbf{6}$$

To compare the complexation behavior of the unsaturated thiacrown ethers with that of the saturated system, the complexation of 18S6 with CF_3COOAg was examined. The reactions of 18S6 with 1, 2, 3, and 4 equiv of CF_3COOAg were carried out individually. When 2 and 4 equiv of CF_3COOAg were added to an acetone solution of 18S6, 2:1 and 4:1 silver(I) complexes, $Ag^I_2(18S6)(CF_3COO)_2$ (**7**) and $Ag^I_4(18S6)(CF_3COO)_4$ (**8**), were obtained as stable colorless prisms in 81% and 75% yields, respectively, whereas the 1:1 and 3:1 metal/macrocycle complexes were not obtained as crystals by the reactions of 18S6 with 1 and 3 equiv of CF_3COOAg. On the other hand, 2:1, 3:1, and 4:1 metal/macrocycle complexes were not obtained when the reactions of **3** with 2, 3, and 4 equiv of CF_3COOAg were examined, respectively. These differences in complexation behavior are perhaps due to the difference in flexibility of the saturated and unsaturated systems.

Crystal Structures. Crystal structures of complexes **5**, **6**, and **7** were determined by X-ray crystallographic analysis (Figures 1 and 2). The selected atomic distances and angles are listed in Table 1.

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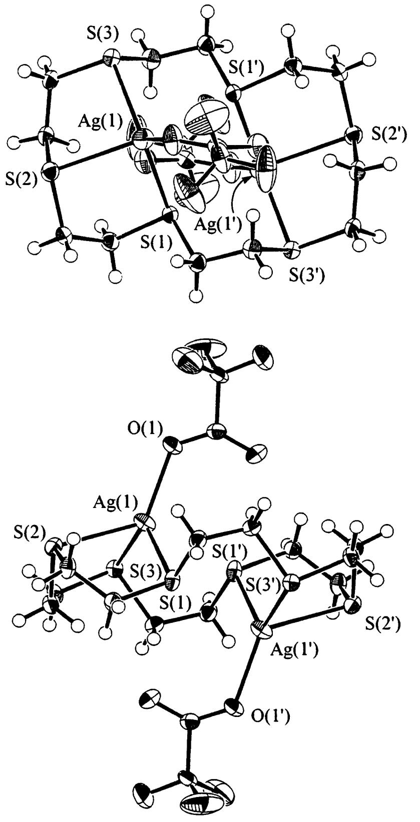

(Side View)

FIGURE 2. ORTEP drawing of $\mathrm{Ag^{I}_2(18S6)(CF_3COO)_2}$ (**7**) showing thermal ellipsoids at 50% probability level.

The ORTEP drawing of **5** shows that a silver atom is present in the cavity of **3** and coordinated by three sulfur atoms of the macrocycle and a trifluoroacetate anion with Ag(1)−S(1) 2.80, Ag(1)−S(3) 2.78, Ag(1)−S(4) 2.81, and Ag(1)−O(1) 2.28 Å. In addition, sulfur atom S(6) is located close to Ag(1) with a distance of 2.92 Å; therefore, it is also considered to coordinate to the silver atom. The angles S(1)−Ag(1)−S(3), S(3)−Ag(1)−S(4), S(4)−Ag(1)···S(6), and S(6)···Ag(1)−S(1) are in the range of 67.9−91.1°, and the average of the angles O(1)−Ag(1)−S is 115.7°. These results show that the geometry around the silver atom has a distorted five-coordinate square pyramidal arrangement.

The crystal structure of **6** shows that host molecule **4** forms a complex with two CF_3COOAg and the two silver atoms and all sulfur atoms are nearly coplanar. The two trifluoroacetate groups are located at the opposite sides of the plane, and the two oxygen atoms of each trifluoroacetate group coordinate to different silver atoms. The bond lengths of Ag(1)−S(1), Ag(1)−S(2), Ag(2)−S(5), and Ag(2)−S(6) are 2.80, 2.78, 2.78, and 2.73 Å, respectively. In addition, sulfur atoms S(3) and S(7) are located close to Ag(1) with distances of 3.11 and 3.12 Å, respectively, and S(4) is located close to Ag(2) with a distance of 2.85 Å. The distance between Ag(1) and Ag(2) is also small at 2.92 Å, which is much smaller than twice the van der Waals radius for silver (3.40 Å) and near to twice the covalent bond radius (2.88 Å).[8]

The ORTEP drawing of $\mathrm{Ag^{I}_2(18S6)(CF_3COO)_2}$ (**7**) shows that 18S6 forms a complex with the two silver atoms. The complex has C_i symmetry in the crystalline state, and the two silver atoms are located at the opposite sides of 18S6. Each of the silver atoms is coordinated by three sulfur atoms and a trifluoroacetate group with Ag(1)−S(1) 2.63, Ag(1)−S(2) 2.64, Ag(1)−S(3) 2.62, and Ag(1)−O(1) 2.22 Å. In addition, S(1′) atom is located close to Ag(1) with a distance of 2.98 Å, so that the geometry around the silver atom has a five-coordinate square pyramidal arrangement. The atomic distance between Ag(1) and Ag(1′) is 4.31 Å, indicating no interaction between them.

Inclusion Behavior in Solution. The ^{1}H NMR spectra of **5** and **6** in acetone-d_6 showed only one singlet at 6.84 and 6.72 ppm, respectively, despite the finding that the silver atoms of complexes **5** and **6** were coordinated with some specified sulfur atoms in the crystal state. These results indicate that there is facile interconversion between the complexing and non-complexing macrocycles in solution. The ^{1}H NMR signals of **1**, **3**, and **4** shifted to the lower field from their original values (6.62, 6.59, and 6.57 ppm, respectively) with the addition of CF_3COOAg. The inclusion behavior of **1**, **3**, and **4** with CF_3COOAg in acetone-d_6 was examined on the basis of the chemical shift values of the singlet signal. The titration plots of **1**, **3**, and **4** with CF_3COOAg are illustrated in Figure 3a. The titration plots of **1** show that the chemical shift changes linearly up to 1 equiv of CF_3COOAg, and the slope changes at 1:1 $[CF_3COOAg]_t/[\mathbf{1}]_t$ ratio. This result indicates that the 1:1 complex of **1** is formed until the ratio reaches 1:1. A linear downfield shift was also observed in the range of $1 < [CF_3COOAg]_t/[\mathbf{1}]_t$ although the slope was gentle, showing that weak interaction with two or more silver ions also exists in solution. In the case of **4**, a distinct inflection point was found at 2:1 $[CF_3COOAg]_t/[\mathbf{4}]_t$ ratio. This means that the 2:1 complex of **4** is stable in solution. However, in the case of **3**, a sharp inflection point was not observed. This result suggests that **3** shows an inclusion behavior intermediate of those of **1** and **4**. It was revealed that unsaturated thiacrown ethers **1** and **4** show selectivity for the inclusion number of silver ions in solution, and the results are in accord with the formation of 1:1 and 2:1 complexes as crystals in the reactions of **1** and **4** with CF_3COOAg.

The silver ion inclusion behavior of 18S6 was also examined for comparison with those of the unsaturated systems. The slope of the titration plots for 18S6 shows complicated changes (Figure 3b). As mentioned before, the reactions of 18S6 with 2 and 4 equiv of CF_3COOAg afforded the 2:1 and 4:1 metal/macrocycle complexes as crystals, respectively. The titration plots show good agreement with the results of the complexation reactions. These results indicate that 18S6 has low selectivity for the inclusion number of silver ions in solution.

The binding constants of **1**, **3**, and **4** with CF_3COOAg were determined by nonlinear least-squares curve fitting[9] using the second-order equilibrium equation for the titration plots of **1**, **3**, and **4**, and the results are shown in Table 2. K_1 values decrease with increasing ring size,

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TABLE 1. Selected Atomic Distances and Angles of Silver Complexes 5, 6, and 7

Ag^I(18-UT-6)(CF$_3$COO) (**5**)		Ag$^I_2$(21-UT-7)(CF$_3$COO)$_2$ (**6**)		Ag$^I_2$(18S6)(CF$_3$COO)$_2$ (**7**)	
		Distances, Å			
Ag(1)−S(1)	2.801(2)	Ag(1)−Ag(2)	2.9205(5)	Ag(1)····Ag(1′)	4.3105(6)
Ag(1)−S(3)	2.777(2)	Ag(1)−S(1)	2.797(1)	Ag(1)−S(1)	2.6346(8)
Ag(1)−S(4)	2.811(2)	Ag(1)−S(2)	2.779(1)	Ag(1)−S(2)	2.6375(9)
Ag(1)···S(6)	2.918(2)	Ag(1)···S(3)	3.112(1)	Ag(1)−S(3)	2.6232(8)
Ag(1)−O(1)	2.280(5)	Ag(1)···S(7)	3.119(1)	Ag(1)···S(1′)	2.9758(8)
		Ag(1)−O(1)	2.314(3)	Ag(1)−O(1)	2.217(3)
		Ag(1)−O(3)	2.263(3)		
		Ag(2)···S(4)	2.845(1)		
		Ag(2)−S(5)	2.775(1)		
		Ag(2)−S(6)	2.733(1)		
		Ag(2)−O(2)	2.297(3)		
		Ag(2)−O(4)	2.286(3)		
		Angles, deg			
S(1)−Ag(1)−S(3)	91.05(6)	Ag(2)−Ag(1)−S(1)	140.79(3)	S(1)−Ag(1)···S(1′)	79.78(3)
S(1)−Ag(1)−S(4)	127.35(6)	Ag(2)−Ag(1)−S(2)	141.08(4)	S(1)−Ag(1)−S(2)	81.76(2)
S(1)−Ag(1)···S(6)	67.85(6)	Ag(2)−Ag(1)···S(3)	79.45(3)	S(1)−Ag(1)−S(3)	114.73(3)
S(3)−Ag(1)−S(4)	70.97(5)	Ag(2)−Ag(1)···S(7)	78.46(2)	S(1′)···Ag(1)−S(2)	138.37(3)
S(3)−Ag(1)···S(6)	127.92(6)	S(1)−Ag(1)−S(2)	69.34(4)	S(1′)···Ag(1)−S(3)	72.15(2)
S(4)−Ag(1)···S(6)	84.85(6)	S(1)−Ag(1)···S(3)	135.10(4)	S(2)−Ag(1)−S(3)	82.47(3)
S(1)−Ag(1)−O(1)	120.4(2)	S(1)−Ag(1)···S(7)	65.98(3)	S(1)−Ag(1)−O(1)	117.41(9)
S(3)−Ag(1)−O(1)	122.0(2)	S(2)−Ag(1)···S(3)	65.84(4)	S(1′)···Ag(1)−O(1)	98.90(7)
S(4)−Ag(1)−O(1)	110.7(2)	S(2)−Ag(1)···S(7)	135.08(4)	S(2)−Ag(1)−O(1)	122.71(7)
S(6)···Ag(1)−O(1)	109.5(2)	S(3)···Ag(1)···S(7)	157.90(4)	S(3)−Ag(1)−O(1)	124.26(9)
		Ag(1)−Ag(2)···S(4)	107.82(3)		
		Ag(1)−Ag(2)−S(5)	174.17(2)		
		Ag(1)−Ag(2)−S(6)	109.30(2)		
		S(4)···Ag(2)−S(5)	70.81(4)		
		S(4)···Ag(2)−S(6)	142.69(4)		
		S(5)−Ag(2)−S(6)	72.63(3)		

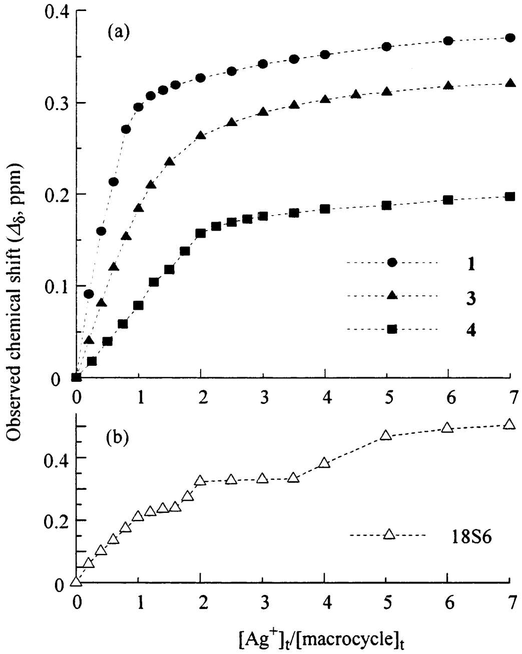

FIGURE 3. ^{1}H NMR shift titration of (a) **1**, **3**, and **4** and (b) 18S6 with CF$_3$COOAg in acetone-d_6 at 27 °C in concentration of the macrocycles at 4.0 × 10^{-3} M.

whereas K_2 increases. Regarding the binding constants with CF$_3$COOAg, K_1 is much larger than K_2 (log $K_1 = 5.1$, log $K_2 = 1.8$) for **1**, whereas it is smaller than K_2 (log $K_1 = 3.2$, log $K_2 = 4.0$) for **4**. The binding constants K_1 (log $K_1 = 4.2$) and K_2 (log $K_2 = 2.5$) of **3** show values intermediate to those of **1** and **4**.

TABLE 2. Binding Constants for Complexation of Unsaturated Thiacrown Ethers 1, 3, and 4 with CF$_3$COOAg in Acetone-d_6[a]

compd	log K_1	log K_2
15-UT-5 (**1**)	5.1 ± 0.3	1.8 ± 0.3
18-UT-6 (**3**)	4.2 ± 0.2	2.5 ± 0.3
21-UT-7 (**4**)	3.2 ± 0.3	4.0 ± 0.2

[a] Corresponding to the general equilibrium: $M + L \rightleftharpoons ML$, $M + ML \rightleftharpoons M_2L$ ($K_1 = [ML]/[M][L]$, $K_2 = [M_2L]/[M][ML]$). The calculated infinite values of the chemical shifts for the (a) 1:1 and (b) 2:1 complexes are obtained as follows. **1**: (a) 6.95, (b) 7.25 ppm; **3**: (a) 6.88, (b) 6.98 ppm; **4**: (a) 6.63, (b) 6.74 ppm.

The distributions of [1:1 complex], [2:1 complex], [macrocycle], and [Ag$^+$] for **1**, **3**, and **4** according to amount of CF$_3$COOAg added were derived from the binding constants, and the results are shown in Figure 4. Figure 4a shows that only the 1:1 complex is formed when up to 1 equiv of CF$_3$COOAg is added to **1**, and a small amount of the 2:1 complex starts to form when more than 1 equiv of CF$_3$COOAg is added. In the case of **3** (Figure 4b), the formation of the 1:1 complex is preferred over that of the 2:1 complex even if the [CF$_3$COOAg]$_t$/[**3**]$_t$ ratio is 2, although the amount of the 2:1 complex formed is larger than that of **1** shown in Figure 4a. In the case of **4**, the 2:1 complex is formed even when less than 1 equiv of CF$_3$COOAg is added to **4**. In addition, when 0.5 < [CF$_3$COOAg]$_t$/[**4**]$_t$, the amount of the 2:1 complex exceeds that of the 1:1 complex.

Electrochemistry. The electrochemical redox behavior of **5**, **6**, and CF$_3$COOAg was examined. Cyclic voltammograms were measured in acetonitrile using a platinum working electrode with a scanning potential range of +1.1 to −1.2 V. Cyclic voltammograms of complexes **5** and **6** showed irreversible oxidation peaks at +0.79 and

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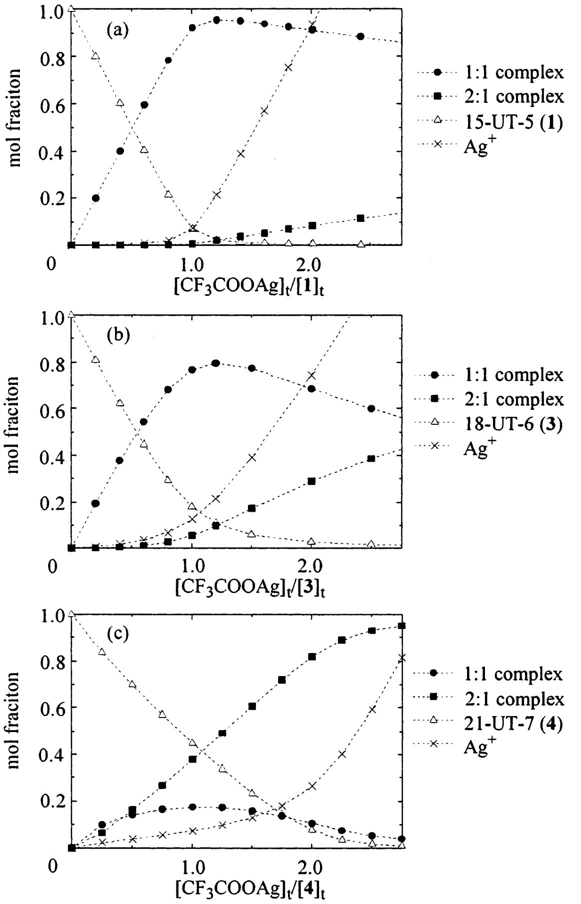

FIGURE 4. Distribution diagram of [1:1 complex], [2:1 complex], [macrocycle], and [Ag$^+$] for (a) **1**, (b) **3**, and (c) **4** according to amount of additive CF_3COOAg.

TABLE 3. Electrochemical Data for Silver Complexes 2, 5, and 6, Unsaturated Thiacrown Ethers 1, 3, and 4, and CF_3COOAg[a]

compd	E_{pa}, V[b]	E_{pc}, V[b]
Ag^I(15-UT-5)(CF_3COO) (**2**)[c]	+0.83	−0.40
Ag^I(18-UT-6)(CF_3COO) (**5**)	+0.79	−0.42
Ag$^I_2$(21-UT-7)(CF_3COO)$_2$ (**6**)	+0.77	−0.46
15-UT-5 (**1**)[c]	+0.79	
18-UT-6 (**3**)[c]	+0.77	
21-UT-7 (**4**)[c]	+0.75	
CF_3COOAg		−0.30

[a] In acetonitrile at a scan rate of 100 mV s^{-1} with 0.1 M n-Bu_4NClO_4 as supporting electrolyte and 1.5 mM samples at a Pt working electrode. [b] Versus Fc/Fc$^+$. [c] Reference 7.

+0.77 V vs Fc/Fc$^+$ and irreversible reduction peaks at −0.42 and −0.46 V, respectively, whereas that of CF_3COOAg showed only an irreversible reduction peak at −0.30 V. These results are listed in Table 3, together with the oxidation and reduction potentials of **1**, **3**, **4**, and **2**.[7] Comparing the oxidation and reduction potentials of the complexes with those of free macrocycles **1**, **3**, and **4**, it was revealed that the macrocycles become difficult to be oxidized by complexation with CF_3COOAg, and CF_3COOAg becomes difficult to be reduced by complexation with the macrocycles.

Conclusions

The reactions of 18- and 21-membered unsaturated thiacrown ethers 18-UT-6 (**3**) and 21-UT-7 (**4**) with CF_3COOAg afforded novel silver(I) complexes Ag^I(18-UT-6)(CF_3COO) (**5**) and Ag$^I_2$(21-UT-7)(CF_3COO)$_2$ (**6**), respectively. The structures of **5** and **6** were confirmed by X-ray crystallographic analysis to include one and two silver atoms in the cavity of the macrocycle, respectively. Examination of the stoichiometry for complexation in solution indicated that **1** and **4** have high selectivity for the inclusion number of silver ions, and **3** shows an inclusion behavior intermediate to those of **1** and **4**. By comparing the oxidation and reduction potentials of complexes **2**, **5**, and **6** with those of free macrocycles **1**, **3**, and **4**, and CF_3COOAg, it was found that **1**, **3**, and **4** become difficult to be oxidized by complexation with CF_3COOAg, and CF_3COOAg becomes difficult to be reduced by complexation with the macrocycle.

Experimental Section

General. Acetone was distilled from $CaSO_4$, and acetonitrile was distilled from CaH_2 prior to use. ^{13}C NMR spectra of Ag$^I_2$(18S6)(CF_3COO)$_2$ (**7**) and Ag$^I_4$(18S6)(CF_3COO)$_4$ (**8**) were measured in DMSO-d_6 besides acetone-d_6 because the complexes were less soluble in acetone-d_6.

Ag^I(18-UT-6)(CF_3COO) (5). An acetone solution (2 mL) of silver trifluoroacetate (53 mg, 0.24 mmol) was added to an acetone solution (30 mL) of 18-UT-6 (**2**) (84 mg, 0.24 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 5 h. Crystallization by slow evaporation of acetone under N_2 stream yielded colorless crystals of Ag^I(18-UT-6)(CF_3COO) (**5**) (86 mg, 63%). Anal. Calcd for $C_{14}H_{12}F_3O_2S_6Ag$: C, 29.53; H, 2.12. Found: C, 29.60; H, 2.16; mp 164.5−166.0 °C (colorless prisms from acetone, decomp); ^{1}H NMR (500 MHz, acetone-d_6) δ 6.77 (12H, s); ^{13}C NMR (125 MHz, acetone-d_6) δ 119.0 (q, J = 290 Hz, $\mathit{C}F_3CO$), 126.3 (s, $H\mathit{C}{=}\mathit{C}H$), 161.4 (q, J = 33 Hz, $CF_3\mathit{C}O$); MS (EI) m/z 348 ($C_{12}H_{12}S_6^+$, 2%), 116 ($C_4H_4S_2^+$, 100%); IR (KBr) ν_{max} 3449, 3021, 1671, 1560, 1545, 1527, 1432, 1283, 1203, 1124, 811, 722, 670 cm^{-1}.

Ag$^I_2$(21-UT-7)(CF_3COO)$_2$ (6). An acetone solution (3 mL) of silver trifluoroacetate (106 mg, 0.48 mmol) was added to an acetone solution (30 mL) of 21-UT-7 (**4**) (99 mg, 0.24 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 5 h. Crystallization by slow evaporation of acetone under N_2 stream yielded colorless crystals of Ag$^I_2$(21-UT-7)(CF_3COO)$_2$ (**6**) (173 mg, 85%). Anal. Calcd for $C_{18}H_{14}F_6O_4S_7Ag_2$: C, 25.48; H, 1.66. Found: C, 25.38; H, 1.58; mp 175.5−177.0 °C (colorless prisms from acetone, decomp); ^{1}H NMR (500 MHz, acetone-d_6) δ 6.72 (14H, s); ^{13}C NMR (125 MHz, acetone-d_6) δ 119.3 (q, J = 290 Hz, $\mathit{C}F_3CO$), 123.2 (s, $H\mathit{C}{=}\mathit{C}H$), 161.3 (q, J = 34 Hz, $CF_3\mathit{C}O$); MS (EI) m/z 406 ($C_{14}H_{14}S_7^+$, 2%), 116 ($C_4H_4S_2^+$, 100%); IR (KBr) ν_{max} 3433, 3026, 1662, 1555, 1437, 1278, 1211, 839, 808, 725, 674, 636 cm^{-1}.

Ag$^I_2$(18S6)(CF_3COO)$_2$ (7). An acetone solution (3 mL) of silver trifluoroacetate (55 mg, 0.25 mmol) was added to an acetone solution (15 mL) of 18S6 (45 mg, 0.12 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 5 h. Crystallization by slow evaporation of acetone under N_2 stream yielded colorless crystals of Ag$^I_2$(18S6)(CF_3COO)$_2$ (**7**) (81 mg, 81%). Anal. Calcd for $C_{16}H_{24}Ag_2F_6O_4S_6$: C, 23.95; H, 3.01. Found: C, 23.85; H, 2.88; mp 211.5−216.0 °C (colorless prisms from acetone, decomp); ^{1}H NMR (500 MHz, acetone-d_6) δ 3.14 (24H, s); ^{13}C NMR (125 MHz, acetone-d_6) δ 31.8 (s, $H_2\mathit{C}{-}\mathit{C}H_2$); ^{13}C NMR (100 MHz, DMSO-d_6) δ 30.5 (s, $H_2\mathit{C}{-}\mathit{C}H_2$), 120.6 (q, J = 292 Hz, $\mathit{C}F_3CO$), 158.3 (q, J = 33 Hz, $CF_3\mathit{C}O$); MS (EI) m/z 360 ($C_{12}H_{24}S_6^+$, 2%), 120 ($C_4H_8S_2^+$, 100%); IR (KBr) ν_{max} 3437, 2906, 1682, 1415, 1206, 1131, 839, 804, 723 cm^{-1}.

Ag$^I_4$(18S6)(CF_3COO)$_4$ (8). An acetone solution (3 mL) of silver trifluoroacetate (113 mg, 0.51 mmol) was added to an acetone solution (15 mL) of 18S6 (46 mg, 0.13 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 5 h. Crystallization by slow evaporation of acetone under N_2 stream yielded colorless crystals of $Ag^{I}_4(18S6)(CF_3COO)_4$ (**8**) (120 mg, 75%). Anal. Calcd for $C_{20}H_{24}Ag_4F_{12}O_8S_6$: C, 19.31; H, 1.94. Found: C, 19.33; H, 1.97; mp 211.0−215.5 °C (colorless prisms from acetone, decomp); ^1H NMR (500 MHz, acetone-d_6) δ 3.20 (24H, s); ^{13}C NMR (125 MHz, acetone-d_6) δ 32.2 (s, $-H_2C\text{-}CH_2\text{-}$); ^{13}C NMR (100 MHz, DMSO-d_6) δ 30.4 (s, $-H_2C\text{-}CH_2\text{-}$), 117.5 (q, $J = 297$ Hz, CF_3CO), 158.3 (q, $J = 31$ Hz, CF_3CO); MS (EI) m/z 360 ($C_{12}H_{24}S_6^+$, 2%), 120 ($C_4H_8S_2^+$, 100%); IR (KBr) ν_{max} 3442, 2902, 1682, 1427, 1264, 1207, 1132, 839, 804, 724 cm^{-1}.

X-ray Structure Determination. Data of X-ray diffraction were collected imaging plate two-dimensional area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) to 2θ max of 55.0°. All of the crystallographic calculations were performed by using teXan software package of the Molecular Structure Corporation. The crystal structure was solved by the direct methods and refined by the full-matrix least squares. All non-hydrogen atoms were refined anisotropically. The experimental details including data collection, data reduction, and structure solution and refinement as well as the atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters have been deposited in Supporting Information.

Crystal Data for 5: $C_{14}H_{12}AgF_3O_2S_6$, fw = 569.47, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 12.5442(7)$ Å, $b = 18.095(1)$ Å, $c = 9.0694$ Å, $V = 2058.6(2)$ Å^3, $Z = 4$, $D_{calc} = 1.837$ g cm^{-3}, μ (Mo Kα) = 16.17 cm^{-1}. A colorless crystal with dimensions of 0.40 × 0.50 × 0.50 mm was used for data collection. A total of 10373 unique reflections were obtained, and 1826 observed reflections [$I > 3\sigma(I)$] were used for refinement to give $R = 0.059$, and $R_w = 0.084$, and R1 = 0.039.

Crystal Data for 6: $C_{18}H_{14}Ag_2F_6O_4S_7$, fw = 848.45, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.176(1)$ Å, $b = 20.820(1)$ Å, $c = 13.058(1)$ Å, $\beta = 98.265(3)$°, $V = 2737.8(4)$ Å^3, $Z = 4$, $D_{calc} = 2.058$ g cm^{-3}, μ (Mo Kα) = 20.26 cm^{-1}. A colorless crystal with dimensions of 0.20 × 0.40 × 0.40 mm was used for data collection. A total of 24871 unique reflections were obtained, and 4877 observed reflections [$I > 3\sigma(I)$] were used for refinement to give $R = 0.123$, and $R_w = 0.115$, and R1 = 0.049.

Crystal Data for 7: $C_{16}H_{24}Ag_2F_6O_4S_6$, fw = 802.45, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.1596(4)$ Å, $b = 10.2036(5)$ Å, $c = 7.6426(5)$ Å, $\alpha = 111.590(6)$°, $\beta = 102.586(2)$°, $\gamma = 99.493(3)$°, $V = 624.05(5)$ Å^3, $Z = 1$, $D_{calc} = 2.135$ g cm^{-3}, μ (Mo Kα) = 21.34 cm^{-1}. A colorless crystal with dimensions of 0.25 × 0.30 × 0.50 mm was used for data collection. A total of 5645 unique reflections were obtained, and 2390 observed reflections [$I > 3\sigma(I)$] were used for refinement to give $R = 0.058$, and $R_w = 0.085$, and R1 = 0.032.

Typical Procedure for ^{1}H NMR Shift Titration. To acetone-d_6 solutions of macrocycle (1×10^{-2} M, 200 μL) in NMR tubes were added required amounts of a acetone-d_6 solution of CF_3COOAg (4×10^{-2} M, 0−350 μL) individually. The volume of the samples was prepared to 550 μL by addition of acetone-d_6 (concentration of macrocycle = 4×10^{-3} M). ^{1}H NMR measurement of the samples was carried out at 27 °C.

Cyclic Voltammetry. Cyclic voltammograms were measured in acetonitrile. A 0.1 M solution of tetra-n-butylammonium perchlorate was used as supporting electrolyte solution. The solid samples were added and dissolved in this solution to yield 1.5 mM concentrations of the respective materials. Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1}. Formal oxidation potentials are given vs the reference system ferrocene/ferrocenium (Fc/Fc$^+$) in volts.

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Supporting Information Available: X-ray crystallographic files in CIF format for **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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