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Unsaturated Thiacrown Ethers: Synthesis, Physical Properties, and Formation of a Silver Complex

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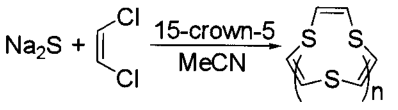
Abstract: The 6-, 9-, 12-, 15-, 18-, 21-, 24-, and 27-membered unsaturated thiacrown ethers **1**−**8** were formed by reaction of *cis*-1,2-dichloroethylene with sodium sulfide in acetonitrile. Crystal structures of **4**−**8** were determined by X-ray crystallography, and it was found that all sulfur atoms of **5**−**8** direct to the inside of the ring (endodentate). All of the ORTEP drawings show that there are cavities in these molecules, and the cavity sizes in **4**−**8** were 1.76, 2.34, 3.48, 4.43, and 5.36 Å, respectively. The UV spectra of **4**−**8** showed absorption maximums at the range of 255−276 nm in acetonitrile, and the absorption maximums of **4**−**8** were found to shift to longer wavelengths by changing the solvent from acetonitrile to cyclohexane. The cyclic voltammograms of **4**−**8** indicate that the larger unsaturated thiacrown ethers were oxidized more easily than the smaller systems, and unsaturated thiacrown ethers were oxidized more easily than corresponding saturated systems. The reaction of **4** with silver trifluoroacetate in acetone afforded the colorless complex $Ag^I(C_2H_2S)_5(CF_3COO)$ **9**. The crystal structure of **9** was determined by X-ray analysis, and it was found that three of the five sulfur atoms bonded to the silver atom.

Introduction

Over the past 20 years, there have been tremendous advances in the chemistry of sulfur-substituted crown ethers, thiacrown ethers.[1,2] Among the differences between crown ethers and thiacrown ethers, the latter are known to coordinate to transition metals[1,3] whereas crown ethers prefer to coordinate with alkaline and alkaline earth metals.[4] On the other hand, unsaturated thiacrown ethers with cis geometry across the carbon−carbon double bonds are considered to be more conformationally restricted than corresponding saturated systems. Therefore, high selectivity toward metals is expected in the formation of metal complexes with unsaturated thiacrown ethers. Among these unsaturated systems, the smallest cyclic compound, 1,4-dithiin, has been widely studied;[5] however, the larger cyclic systems have only rarely been investigated. Very recently, two unsaturated thiacrown ethers, 9- and 18-membered cyclic compounds, which are fused with benzene rings, were synthesized by Nakayama and co-workers.[6] However, little is known about their chemical and physical properties. In this paper, we report the synthesis, structures, redox properties, and formation with silver complex of novel unsaturated thiacrown ethers without substituents.



1: n = 0; 1,4-dithiin
2: n = 1; 9-UT-3
3: n = 2; 12-UT-4
4: n = 3; 15-UT-5
5: n = 4; 18-UT-6
6: n = 5; 21-UT-7
7: n = 6; 24-UT-8
8: n = 7; 27-UT-9

Results and Discussion

Synthesis. When *cis*-1,2-dichloroethylene was treated with sodium sulfide in acetonitrile at 50 °C, 6-, 9-, 12-, 15-, 18-, 21-, 24-, and 27-membered unsaturated thiacrown ethers (1,4-dithiin, 9-UT-3, 12-UT-4, 15-UT-5, 18-UT-6, 21-UT-7, 24-UT-8, and 27-UT-9, respectively)[7,8] **1**−**8** were formed, although the yields were low (18% total yield) (Table 1). Even attempts to

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(7) In this paper, unsaturated thiacrown ethers are abbreviated as x-UT-y (UT, *u*nsaturated *t*hiacrown ether; x, *x*-membered ring; y, number of sulfur atom).

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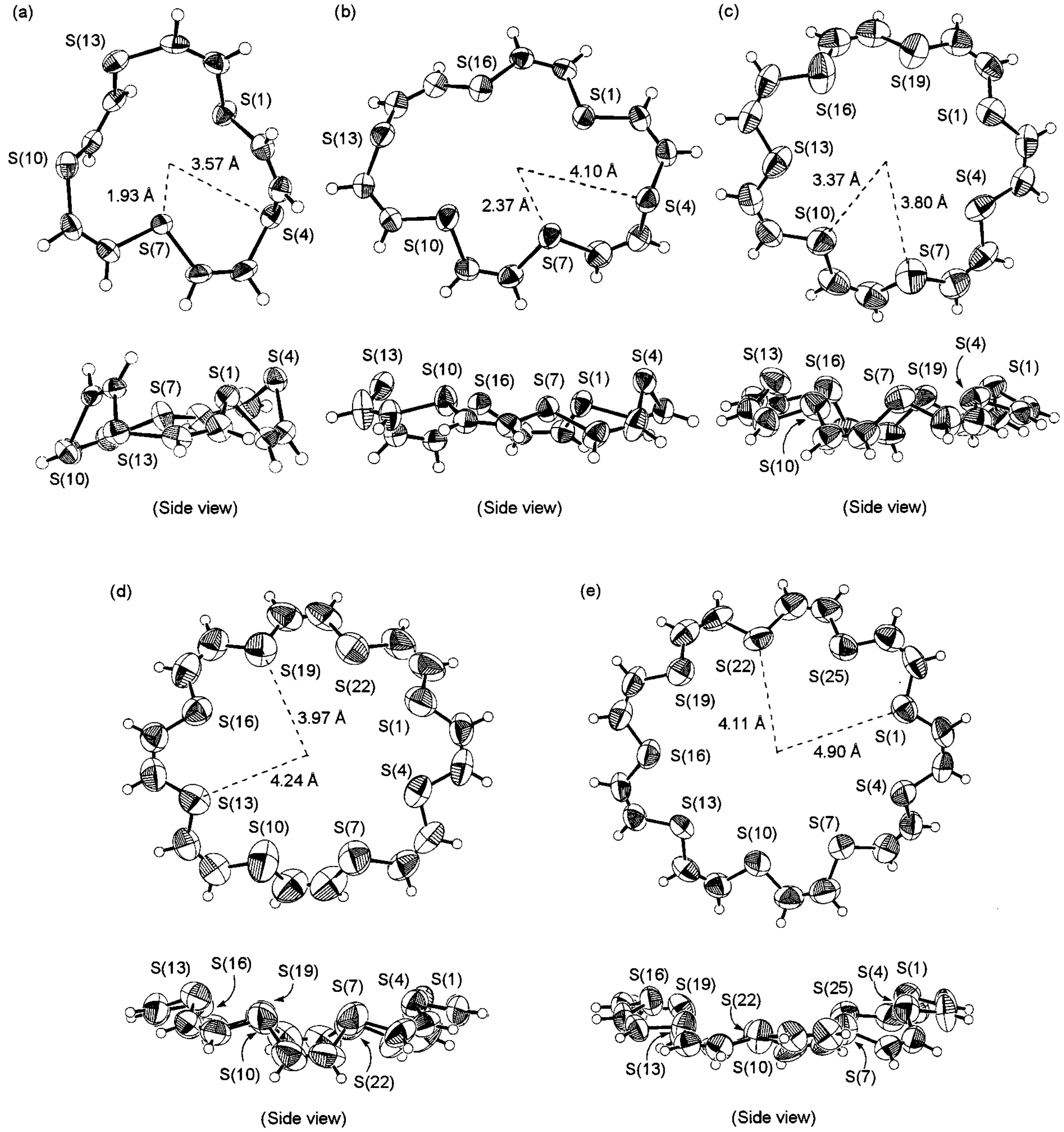

Figure 1. ORTEP drawings of (a) 15-UT-5 (**4**), (b) 18-UT-6 (**5**), (c) 21-UT-7 (**6**), (d) 24-UT-8 (**7**), and (e) 27-UT-9 (**8**) showing thermal ellipsoids at 50% probability level. Shortest and longest distances between the center of the molecule and the sulfur atoms are denoted.

react *cis*-1,2-dichloroethylene with sodium sulfide in the presence of Cs_2CO_3, a method useful for preparing saturated thiacrown ethers,[2,9] yields were hardly improved. The low yield may be due to the heterogeneous reaction system; i.e., sodium sulfide is less soluble in acetonitrile. In the presence of 0.1 equiv of 15-crown-5 as a phase-transfer catalyst, the reaction proceeded smoothly even at room temperature, and the total yield of unsaturated thiacrown ethers was improved to 32% (**1**/**2**/**3**/**4**/**5**/**6**/**7**/**8** = 44/4/trace/6/19/14/8/5). The total yield was increased to 40% when 0.4 equiv of 15-crown-5 was added to the reaction system; however, no further improvement was observed when 1.0 equiv of 15-crown-5 was added. Among these, **1** and **4**−**8** could be isolated by silica gel column chromatography (hexane/acetone = 2/1). In this reaction, fluffy amorphous solids, which were not soluble in organic and aqueous phase, were also obtained. The solids may be electroconducting poly(vinylene sulfides) reported by Ikeda and coworkers.[10]

Table 1. Reaction of *cis*-1,2-Dichloroethylene with Sodium Sulfide in Acetonitrile

run	15-crown-5 (equiv)	temp (°C)	time (h)	total (%)	yields[a] **1**/**2**/**3**/**4**/**5**/**6**/**7**/**8**
1		40	45	18	48/6/trace/8/14/10/8/6
2	0.1	rt	45	32	44/4/trace/6/19/14/8/5
3	0.4	rt	45	40	44/3/trace/4/18/16/10/5

[a] Yields were determined by ^1H NMR spectra.

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(8) 9-UT-3 (**2**) and 12-UT-4 (**3**) were identified by ^1H NMR, ^{13}C NMR, and GC/MS for the mixture of **2** and **3**.

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Table 2. Summary of X-ray Crystallographic Data

	15-UT-5 (**4**)	18-UT-6 (**5**)	21-UT-7 (**6**)	24-UT-8 (**7**)	27-UT-9 (**8**)
empirical formula	$C_{10}H_{10}S_5$	$C_{12}H_{12}S_6$	$C_{14}H_{14}S_7$	$C_{16}H_{16}S_8$	$C_{18}H_{18}S_9$
formula weight	290.49	348.59	406.68	464.78	522.88
crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$Pbca$ (No. 61)	$Pbca$ (No. 61)	$P2_1/n$ (No. 14)
a, Å	9.7111(7)	8.1989(4)	17.1915(6)	17.889(1)	12.5632(8)
b, Å	14.1165(6)	18.322(1)	19.9131(6)	21.852(1)	15.824(1)
c, Å	10.2523(6)	11.0518(7)	11.2108(4)	11.4800(7)	12.793(1)
β, deg	113.659(1)	107.835(1)			100.001(2)
V, Å^3	1287.3(1)	1580.4(1)	3837.9(2)	4487.6(5)	2504.6(3)
Z	4	4	8	8	4
F(000)	600.00	720.00	1680.00	1920.00	1080.00
D_{calc}, g/cm^3	1.499	1.465	1.408	1.376	1.387
T, °C	23	23	23	23	23
crystal size, nm	0.60 × 0.50 × 0.40	0.40 × 0.50 × 0.40	0.40 × 0.50 × 0.30	0.40 × 0.35 × 0.13	0.45 × 0.50 × 0.50
μ (Mo Kα), cm^{-1}	8.64	8.44	8.11	7.93	7.99
$2\theta_{max}$, deg	54.9	55.0	55.0	55.0	55.0
no. of reflns measd	12361	14792	34982	21025	13448
no. of reflns obsd	2433[$I > 3.00\sigma(I)$]	2967[$I > 3.00\sigma(I)$]	1859[$I > 3.00\sigma(I)$]	3620[$I > 0.00\sigma(I)$]	1766[$I > 3.00\sigma(I)$]
no. of variables	136	163	190	217	244
R^a; $R_w{}^b$	0.078; 0.103	0.136; 0.113	0.081; 0.106	0.103; 0.103	0.106; 0.123
R1^c	0.036	0.046	0.042	0.038	0.055

[a] $R = \sum(F_o{}^2 - F_c{}^2)/\sum F_o{}^2$. [b] $R_w = (\sum\omega(F_o{}^2 - F_c{}^2)^2/\sum\omega(F_o{}^2))^{1/2}$; $\omega = 1/\sigma^2(F_o)$. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

Table 3. Selected Bond Distances and Angles of **4**−**8**

15-UT-5 (**4**)		18-UT-6 (**5**)		21-UT-7 (**6**)		24-UT-8 (**7**)		27-UT-9 (**8**)	
				Distances, Å					
S(1)−C(2)	1.743(2)	S(1)−C(2)	1.744(2)	S(1)−C(2)	1.752(5)	S(1)−C(2)	1.692(8)	S(1)−C(2)	1.698(9)
S(1)−C(15)	1.758(2)	S(1)−C(18)	1.743(2)	S(1)−C(21)	1.739(5)	S(1)−C(24)	1.725(8)	S(1)−C(27)	1.76(1)
S(4)−C(3)	1.755(2)	S(4)−C(3)	1.762(3)	S(4)−C(3)	1.742(5)	S(4)−C(3)	1.750(7)	S(4)−C(3)	1.730(10)
S(4)−C(5)	1.761(3)	S(4)−C(5)	1.749(3)	S(4)−C(5)	1.743(5)	S(4)−C(5)	1.707(8)	S(4)−C(5)	1.725(9)
S(7)−C(6)	1.741(2)	S(7)−C(6)	1.736(3)	S(7)−C(6)	1.732(6)	S(7)−C(6)	1.749(8)	S(7)−C(6)	1.729(9)
S(7)−C(8)	1.743(2)	S(7)−C(8)	1.741(3)	S(7)−C(8)	1.738(6)	S(7)−C(8)	1.690(8)	S(7)−C(8)	1.739(9)
S(10)−C(9)	1.753(3)	S(10)−C(9)	1.743(2)	S(10)−C(9)	1.738(5)	S(10)−C(9)	1.722(8)	S(10)−C(9)	1.700(9)
S(10)−C(11)	1.749(2)	S(10)−C(11)	1.725(3)	S(10)−C(11)	1.730(6)	S(10)−C(11)	1.723(8)	S(10)−C(11)	1.733(8)
S(13)−C(12)	1.749(2)	S(13)−C(12)	1.759(3)	S(13)−C(12)	1.722(6)	S(13)−C(12)	1.717(7)	S(13)−C(12)	1.729(8)
S(13)−C(14)	1.746(3)	S(13)−C(14)	1.757(3)	S(13)−C(14)	1.741(5)	S(13)−C(14)	1.737(8)	S(13)−C(14)	1.730(8)
		S(16)−C(15)	1.740(2)	S(16)−C(15)	1.757(5)	S(16)−C(15)	1.721(8)	S(16)−C(15)	1.740(8)
		S(16)−C(17)	1.755(2)	S(16)−C(17)	1.725(5)	S(16)−C(17)	1.713(8)	S(16)−C(17)	1.732(8)
				S(19)−C(18)	1.740(5)	S(19)−C(18)	1.706(8)	S(19)−C(18)	1.724(9)
				S(19)−C(20)	1.725(5)	S(19)−C(20)	1.682(8)	S(19)−C(20)	1.709(10)
						S(22)−C(21)	1.690(8)	S(22)−C(21)	1.759(9)
						S(22)−C(23)	1.718(8)	S(22)−C(23)	1.72(1)
								S(25)−C(24)	1.722(9)
								S(25)−C(26)	1.69(1)
				Angles, deg					
C(15)−S(1)−C(2)	100.1(1)	C(18)−S(1)−C(2)	101.5(1)	C(21)−S(1)−C(2)	101.7(2)	C(24)−S(1)−C(2)	105.5(4)	C(27)−S(1)−C(2)	104.0(5)
C(3)−S(4)−C(5)	101.2(1)	C(3)−S(4)−C(5)	100.7(1)	C(3)−S(4)−C(5)	103.0(3)	C(3)−S(4)−C(5)	100.8(4)	C(3)−S(4)−C(5)	103.8(5)
C(6)−S(7)−C(8)	101.2(1)	C(6)−S(7)−C(8)	102.8(1)	C(6)−S(7)−C(8)	103.1(3)	C(6)−S(7)−C(8)	103.6(4)	C(6)−S(7)−C(8)	102.8(5)
C(9)−S(10)−C(11)	102.8(1)	C(9)−S(10)−C(11)	102.1(1)	C(9)−S(10)−C(11)	103.5(3)	C(9)−S(10)−C(11)	104.2(4)	C(9)−S(10)−C(11)	103.2(4)
C(12)−S(13)−C(14)	107.6(1)	C(12)−S(13)−C(14)	100.3(2)	C(12)−S(13)−C(14)	100.7(3)	C(12)−S(13)−C(14)	100.5(4)	C(12)−S(13)−C(14)	103.9(4)
		C(15)−S(16)−C(17)	101.0(1)	C(15)−S(16)−C(17)	102.5(3)	C(15)−S(16)−C(17)	102.8(4)	C(15)−S(16)−C(17)	101.2(4)
				C(18)−S(19)−C(20)	103.4(3)	C(18)−S(19)−C(20)	103.4(4)	C(18)−S(19)−C(20)	101.7(5)
						C(21)−S(22)−C(23)	106.5(4)	C(21)−S(22)−C(23)	103.4(5)
								C(24)−S(25)−C(26)	101.2(5)

The ^{1}H and ^{13}C NMR signals of the unsaturated thiacrown ethers exhibited lower field shifts with an increase in the ring size from **1** to **4** in $CDCl_3$ (^{1}H NMR (ppm): **1**, 6.21; **2**, 6.27; **3**, 6.43; **4**, 6.48. ^{13}C NMR (ppm): **1**, 121.2; **2**, 123.8; **3**, 126.1; **4**, 126.9) and upper field shifts with an increase in the ring size from **4** to **8** in $CDCl_3$ (^{1}H NMR (ppm): **5**, 6.40; **6**, 6.33; **7**, 6.30; **8**, 6.28. ^{13}C NMR (ppm): **5**, 125.3; **6**, 123.6; **7**, 122.4; **8**, 121.5). These results suggest that the electron density of the olefin moieties increases with increasing ring size from **4** to **8** and decreasing ring size from **4** to **1**.

Crystal Structures. Earlier structural work on saturated thiacrown ethers revealed that sulfur−sulfur 1,4-interactions disfavor gauche placement at S−C−C−S bonds.[11,12,13] In these cases, electron−electron repulsion between sulfur atoms destabilizes gauche placement. The unsaturated thiacrown ethers synthesized in this study are a fixed cis form; therefore, it is interesting to observe the conformational change from saturated thiacrown ethers, whose carbon−carbon single bonds can rotate freely, to unsaturated thiacrown ethers. The crystal structures of 15-, 18-, 21-, 24-, and 27-membered unsaturated thiacrown ethers **4**−**8** were determined by X-ray crystallographic analysis (Figure 1). The crystallographic data, selected bond angles, and bond lengths for these X-ray structures are summarized in Tables 2 and 3. All of the ORTEP drawings show that there are cavities in these molecules, and the sulfur atoms are nearly coplanar. In

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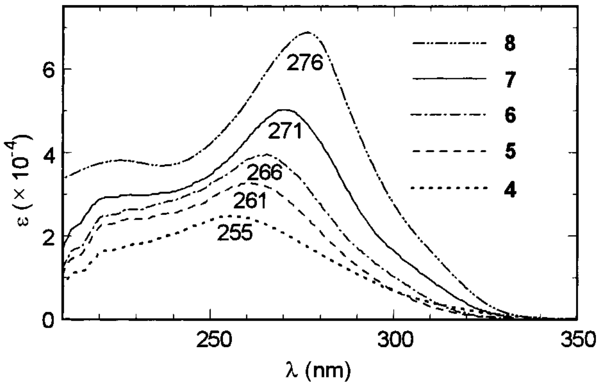


Figure 2. UV spectra of 15-UT-5 (**4**), 18-UT-6 (**5**), 21-UT-7 (**6**), 24-UT-8 (**7**), and 27-UT-9 (**8**) in acetonitrile.

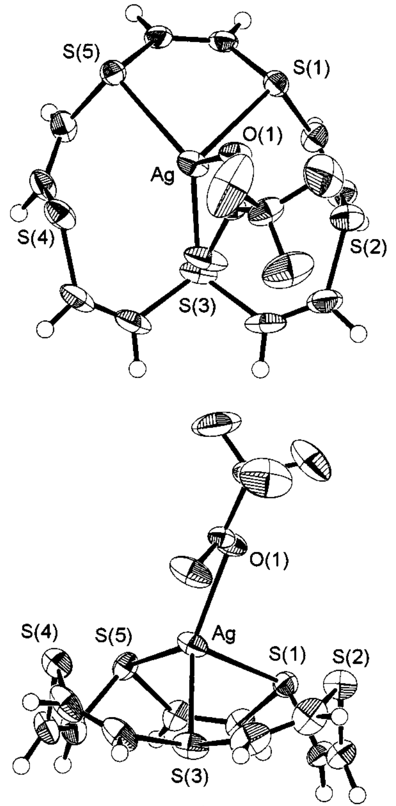
Table 4. Spectral Data of **4**−**8** in Acetonitrile, Ethanol, and Cyclohexane

	λ_{max}, nm (ϵ, M^{-1}cm^{-1})		
compd	acetonitrile	ethanol	cyclohexane
4	255 (24 000)	260 (22 000)	267 (16 000)
5	261 (33 000)	267 (27 000)	271 (22 000)
6	266 (40 000)	268 (32 000)	274[a]
7	271 (50 000)	274 (49 000)	277[a]
8	276 (67 000)	277 (51 000)	283[a]

[a] Molar absorption coefficient has not been determined due to insolubility, and the spectra were measured in saturated solutions.

the crystal structure of **5**, all of the sulfur atoms are oriented toward the inside of the ring (endodentate) whereas the corresponding thiacrown ether, 1,4,7,10,13,16-hexathiacyclooctadecane (18S6), has four endodentate and two exodentate sulfur atoms in the crystalline state.[12,13] In the crystal structures of **6**−**8**, all sulfur atoms are endodentate. The C−S bond lengths in **4** (1.74−1.76 Å) and **5** (1.74−1.76 Å) are shorter than those in 15S5 (1.80−1.95 Å)[12] and 18S6 (1.80−1.96 Å).[12,13] The bond angles in the crystal structures of **4**−**8** are almost strain-free (**4**: S−C−C, 121.7−132.4°; C−S−C, 100.1−107.6°. **5**: S−C−C, 120.8−124.3°; C−S−C, 100.3−102.8°. **6**: S−C−C, 120.7−123.5°; C−S−C, 100.7−103.5°. **7**: S−C−C, 120.3−124.5°; C−S−C, 100.5−106.5°. **8**: S−C−C, 120.4−125.0°; C−S−C, 101.2−104.0°). The most interesting point of these structures is the size of the cavity. The distances between the center of the molecule and the sulfur atoms in **4** and **5** are 1.94−3.57 (average, 2.73) and 2.37−4.07 (average, 3.01) Å, respectively, which are shorter than those in saturated systems [15S5, 3.44−3.99 (average, 3.58)[12] Å; 18S6, 2.36−4.55 (average, 3.56)[12,13] Å]. Those distances in **6**−**8** are 3.37−3.80 (average, 3.59), 3.97−4.24 (average, 4.06), and 4.11−4.90 (average, 4.53) Å, respectively. From those distances and van der Waals radii of sulfur atoms, the cavity sizes in **4**−**8** were estimated to be 1.76, 2.34, 3.48, 4.43, and 5.36 Å, respectively, at the inside of the sulfur atoms.

UV Spectra of 4−8. The UV spectrum of **4** shows an absorption maximum at 255 nm (ϵ 2.4 × 10^4) in acetonitrile, as shown in Figure 2. With an increase in the ring size, the absorption maximums shift to a longer wavelength and the extinction coefficients increase; the UV spectra of larger unsaturated thiacrown ethers **5**−**8** show absorption maximums at 261 (ϵ 3.3 × 10^4), 266 (ϵ 4.0 × 10^4), 271 (ϵ 5.0 × 10^4), and 276 (ϵ 6.7 × 10^4) nm, respectively. This tendency of the shifts of absorption maximums can be explained in terms of delocalization; the excited state would be more stabilized by delocalization of the unpaired electron in the larger systems. The UV spectra of **4** in ethanol and cyclohexane show absorption maximums at 260 (ϵ 2.2 × 10^4) and 267 (ϵ 1.6 × 10^4) nm, respectively, as shown in Table 4. The absorption maximums of **5**−**8** also shift to longer wavelengths in nonpolar solvent, and the extinction coefficients decrease with a decrease in the polarity of the solvent. Thus, the absorptions can be assigned to n → π* transitions.



(Side view)

Figure 3. ORTEP drawing of Ag^{I}(15-UT-5)(CF_3COO) (**9**) showing thermal ellipsoids at 50% probability level. Selected bond lengths (Å) and angles (deg): Ag−O(1), 2.280(3); Ag−S(1), 2.747(1); Ag−S(3), 2.633(1); Ag−S(5), 2.685(1); S(1)−Ag−S(3), 100.50(3); S(1)−Ag−S(5), 75.41 (3); S(3)−Ag−S(5), 112.66(3); S(1)−Ag−O(1), 101.82(8); S(3)−Ag−O(1), 123.78(7); S(5)−Ag−O(1), 122.69(7).

Electrochemistry of 4−8. The electrochemical oxidation of unsaturated thiacrown ethers was examined. A cyclic voltammogram of **4** was measured in acetonitrile at a platinum working electrode and showed an irreversible oxidation peak at +0.79 V versus Fc/Fc^{+} with a scanning potential range of +2.0 to −2.0 V. The reduction peak was not observed in this scanning potential range. The cyclic voltammograms of **5**−**8** also showed irreversible oxidation peaks at +0.77, +0.75, +0.60, and +0.55 V, respectively. These results indicate that the larger unsaturated thiacrown ethers would be oxidized more easily than the smaller systems, probably due to the effect of delocalization of the resulting cation. A cyclic voltammogram of 18S6 was measured to compare the oxidation potential. An irreversible oxidation peak was observed at +1.05 V. It was found that unsaturated thiacrown ethers are oxidized easily than saturated systems.

Silver Complex with 15-UT-5 (4). The reaction of **4** with silver trifluoroacetate in acetone gave the colorless complex Ag^{I}(15-UT-5)(CF_3COO) (**9**) in 95% yield. The crystal structure of **9** was determined by X-ray analysis (Figure 3). Ag^{I} has a distorted tetrahedral geometry and is coordinated by three sulfur atoms of the macrocycle and a trifluoroacetate anion. The bond angles S(1)−Ag−S(5), S(1)−Ag−S(3), and S(3)−Ag−S(5) are 75.4, 100.5, and 112.7°, respectively. The silver−sulfur bond distances range from 2.63 to 2.75 Å, and the Ag···S(2) and

Ag···S(4) distances are 3.36 and 2.87 Å, respectively. The distorted geometry may be due to Ag···S(4) interaction, since the S(4) atom is close to the Ag^I center. Cyclic voltammetry of **9** in acetonitrile at a platinum working electrode shows irreversible oxidation and reduction peaks at +0.80 and −0.27 V versus Fc/Fc^+, respectively, with a scanning potential range of +2.0 to −2.0 V. The results indicate that the oxidized and reduced products are unstable in acetonitrile. In the ^1H NMR spectra, five olefins of the ligand were observed equivalently in acetone-d_6, even at 180 K (300 K, 6.88 ppm; 180 K, 7.09 ppm), and the results show that there is facile interconversion between the coordinated sulfur atoms and noncoordinated sulfur atoms in the solution.

Conclusions

Novel unsaturated thiacrown ethers (**1**−**8**) were synthesized by reaction of *cis*-1,2-dichloroethylene with sodium sulfide. The structures of **4**−**8** were determined by X-ray crystallographic analysis. The UV spectra and the cyclic voltammograms of the unsaturated thiacrown ethers (**4**−**8**) show that the excited states and electrochemically oxidized species of lager unsaturated thiacrown ethers are liable to be stabilized by delocalization more easily than smaller unsaturated ones. Comparing the oxidation potential of unsaturated thiacrown ether with corresponding saturated thiacrown ether, it was found that unsaturated thiacrown ethers were oxidized more easily than saturated systems. The formation of a silver complex with **4** was examined in which three of the five sulfur atoms bonded to the silver atom in the crystalline state.

Experimental Section

General Information. Acetonitrile and cyclohexane were distilled from CaH_2, and acetone was distilled from $CaSO_4$ prior to use. Commercially available 95% ethanol was used without further purification. Column chromatography was performed with Merk 7734 Kieselgel 60. Melting points were determined on a Yamato MP-21 melting point apparatus. UV−visible spectra were measured on a Hitachi U-3500 spectrometer. IR spectra were measured on a Perkin-Elmer Spectrum GX. ^1H and ^{13}C spectra were recorded on a JEOL JNM-EX-500 FT NMR system. Mass spectra (MS) were determined on a JEOL GCMATE.

Synthesis of Unsaturated Thiacrown Ethers. Ground $Na_2S{\cdot}9H_2O$ (6.64 g, 27.6 mmol) and 15-crown-5 (2.43 g, 11.0 mmol) was suspended in 230 mL of acetonitrile. A solution of *cis*-1,2-dichloroethylene (4.50 g, 46.4 mmol) in acetonitrile (40 mL) was added dropwise to the suspension with stirring for 1 h. After additional stirring for 45 h, the reaction mixture was filtered, and the filtrate was concentrated in vacuo. The residue was extracted with AcOEt, washed with H_2O, and dried over $MgSO_4$. The products were isolated by silica gel column chromatography (hexane/acetone = 2/1; R_f: **1**,[5a,b] 0.80; **4**, 0.52; **5**, 0.30; **6**, 0.18; **7**, 0.07; **8**, 0.04).

(*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13-Pentathiacyclopentadeca-2,5,8,11,14-pentaene (15-UT-5) (4): mp 128−129 °C (colorless prisms from dichloromethane); ^1H NMR (500 MHz, $CDCl_3$) δ 6.48 (10H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 126.9; MS (EI) *m*/*z* 290 (M^+, 17%), 116 ($C_4H_4S_2^+$, 100%); IR (KBr) ν_{max} 3025, 3009, 2998, 1555, 1525, 1314, 1293, 1283, 854, 810, 706, 680, 659, 448, 411 cm^{-1}; UV (CH_3CN) λ_{max} 255 (ϵ 2.4 × 10^4) nm, (EtOH) λ_{max} 260 (ϵ 2.2 × 10^4) nm, (cyclohexane) λ_{max} 267 (ϵ 1.6 × 10^4) nm. Anal. Calcd for $C_{10}H_{10}S_5$: C, 41.34; H, 3.47. Found: C, 41.16; H, 3.35.

(*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16-Hexathiacyclooctadeca-2,5,8,11,14,17-hexaene (18-UT-6) (5): mp 165−166 °C (colorless prisms from dichloromethane); ^1H NMR (500 MHz, $CDCl_3$) δ 6.40 (12H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 125.3; MS (EI) *m*/*z* 348 (M^+, 8%), 116 ($C_4H_4S_2^+$, 100%); IR (KBr) ν_{max} 3015, 1547, 1525, 1282, 811, 721, 666, 641, 540, 450, 365 cm^{-1}; UV (CH_3CN) λ_{max} 261 (ϵ 3.3 × 10^4) nm, (EtOH) λ_{max} 267 (ϵ 2.7 × 10^4) nm, (cyclohexane) λ_{max} 271 (ϵ 2.2 × 10^4) nm. Anal. Calcd for $C_{12}H_{12}S_6$: C, 41.34; H, 3.47. Found: C, 41.34; H, 3.48.

(*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16,19-Heptathiacycloheneicosa-2,5,8,11,14,17,20-heptaene (21-UT-7) (6): mp 195−196 °C (colorless prisms from acetone); ^1H NMR (500 MHz, $CDCl_3$) δ 6.33 (14H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 123.6; MS (EI) *m*/*z* 406 (M^+, 7%), 116 ($C_4H_4S_2^+$, 100%); IR (KBr) ν_{max} 3026, 1556, 1277, 810, 716, 673, 657, 636, 535, 400 cm^{-1}; UV (CH_3CN) λ_{max} 266 (ϵ 4.0 × 10^4) nm, (EtOH) λ_{max} 268 (ϵ 3.2 × 10^4) nm, (cyclohexane) λ_{max} 274 nm. Anal. Calcd for $C_{14}H_{14}S_7$: C, 41.34; H, 3.47. Found: C, 41.32; H, 3.39.

(*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16,19,22-Octathiacyclotetracosa-2,5,8,11,14,17,20,23-octaene (24-UT-8) (7): mp 190−192 °C (colorless prisms from acetone, dec); ^1H NMR (500 MHz, $CDCl_3$) δ 6.30 (16H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.4; MS (EI) *m*/*z* 464 (M^+, 3%), 116 ($C_4H_4S_2^+$, 100%); IR (KBr) ν_{max} 3026, 1558, 1272, 808, 725, 657, 625, 539, 410 cm^{-1}; UV (CH_3CN) λ_{max} 271 (ϵ 5.0 × 10^4) nm, (EtOH) λ_{max} 274 (ϵ 4.9 × 10^4) nm, (cyclohexane) λ_{max} 277 nm. Anal. Calcd for $C_{16}H_{16}S_8$: C, 41.34; H, 3.47. Found: C, 41.40; H, 3.48.

(*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16,19,22,25-Nonathiacycloheptacosa-2,5,8,11,14,17,20,23,26-nonaene (27-UT-9) (8): mp 202−203 °C (colorless prisms from acetone, dec); ^1H NMR (500 MHz, $CDCl_3$) δ 6.28 (18H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 121.5; MS (EI) *m*/*z* 522 (M^+, 3%), 116 ($C_4H_4S_2^+$, 100%); IR (KBr) ν_{max} 3034, 1604, 1562, 1272, 871, 807, 720, 656, 624, 542 cm^{-1}; UV (CH_3CN) λ_{max} 276 (ϵ 6.7 × 10^4) nm, (EtOH) λ_{max} 277 (ϵ 5.1 × 10^4) nm, (cyclohexane) λ_{max} 283 nm. Anal. Calcd for $C_{18}H_{18}S_9$: C, 41.34; H, 3.47. Found: C, 41.29; H, 3.45.

Synthesis of Silver Complex with 15-UT-5. A solution of silver trifluoroacetate (58 mg, 0.26 mmol) in acetone (3 mL) was added to a solution of 15-UT-5 (**4**) (70 mg, 0.24 mmol) in acetone (15 mL) under nitrogen. The reaction mixture was stirred at room temperature for 3 h. Crystallization by slow evaporation of acetone yielded colorless crystals of Ag^I(15-UT-5)(CF_3COO) (**9**) (117 mg, 95%).

Ag^I(15-UT-5)(CF_3COO) (9): mp 176−177 °C (colorless prisms from acetone, dec); ^1H NMR (500 MHz, acetone-d_6) δ 6.90 (10H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 119.0 (q, J = 293 Hz, CF_3CO), 127.5 (HC=CH), 161.7 (q, J = 33 Hz, CF_3CO); MS (EI) *m*/*z* 290 ($C_{10}H_{10}S_5^+$, 3%), 116 ($C_4H_4S_2^+$, 100%); IR (KBr) ν_{max} 3026, 3010, 2999, 1682, 1556, 1525, 1432, 1315, 1293, 1283, 1208, 1032, 854, 839, 810, 707, 680, 659, 649, 448 cm^{-1}. Anal. Calcd for $C_{12}H_{10}F_3O_2S_5Ag$: C, 28.18; H, 1.97. Found: C, 28.18; H, 1.94.

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 to this solution to yield 1.5 mM concentrations of the respective materials. Cyclic voltammograms were recorded at scan rate of 100 mV s^{-1}. Formal oxidation potentials are given versus the reference system ferrocene/ferrocenium (Fc/Fc^+) in volts.

X-ray Structure Determination. Data of X-ray diffraction were collected by Rigaku RAXIS-RAPID imaging plate two-dimensional area detector using graphite-monochromated Mo Kα radiation (λ = 0.710 70 Å) to $2\theta_{max}$ of 55.0°. All of the crystallographic calculations were performed by using teXan software package of the Molecular Structure Corp. 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 summary of the fundamental crystal data and experimental parameters for structure determinations is given in Table 2. 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 the Supporting Information.

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Supporting Information Available: X-ray crystallographic files (CIF) for **4**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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