Synthesis of Novel Thiacrown Ethers Containing Alkanone Building Blocks and Complexation with Silver(I). Molecular Structures of 3,6,9-Trithiacyclodecanone, 3,6,9-Trithiacycloundecanone, and 4,7,10-Trithiacyclododecanone

Jilles J. H. Edema,[†] Jan Buter,[†] Franck S. Schoonbeek,[†] Richard M. Kellogg,*,[†] Fre van Bolhuis,[‡] and Anthony L. Spek[§]

Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands, Molecular Structure Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands, and Department of Crystal and Structural Chemistry, Bijvoet Research Center, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

Cyclization of 3-thiapentane-1,5-dithiol (**4**) as its cesium dithiolate with 1,3-dichloropropanone (**1**) gives in 72% yield the cyclic thioether 3,6,9-trithiadecanone ($C_7H_{12}OS_3$, **5**). Crystals are white. Crystal data for **5** at 130 K: monoclinic, space group $P2_1$, with $a = 7.145(1)$ Å, $b = 5.310(1)$ Å, $c = 11.932(1)$ Å, $\beta = 96.57(1)°$, $Z = 2$, $R = 0.024$, and $R_w = 0.032$ for 1640 reflections ($I > 3.0\sigma(I)$). Reaction of **4** with 1,4-dichlorobutanone (**2**) affords in 52% yield the nonsymmetric 3,6,9-trithiaundecanone ($C_8H_{14}OS_3$, **6**). Crystals are white. Crystal data for **6** at 100 K: triclinic, space group $P\bar{1}$, with $a = 5.408(4)$ Å, $b = 7.366(3)$ Å, $c = 13.581(4)$ Å, $\alpha = 80.87(3)°$, $\beta = 78.68(5)°$, $\gamma = 69.79(5)°$, $Z = 2$, $R = 0.074$, and $R_w = 0.095$ for 2105 reflections ($I > 2.5\sigma(I)$). Reaction of **4** with 1,5-dichloropentan-3-one (**3**) resulted in formation of 4,7,10-trithiadodecanone ($C_9H_{16}O_3S$, **7**) in 63% yield. Crystals are white. Crystal data for **7** at 298 K: orthorhombic, space group *Pnma*, with $a = 15.4077(3)$ Å, $b = 15.3536(17)$ Å, $c = 4.9889(11)$ Å, $Z = 4$, $R = 0.072$, and $R_w = 0.080$ for 740 reflections ($I > 2.5\sigma(I)$). Conductometric titrations of AgOTf in MeCN and THF with **5–7** showed that, dependent on solvent and concentration, in solution 1:1 and 3:2 (ligand:Ag$^+$) adducts are formed.

Introduction

The well-known ability of macrocyclic thioethers to bind easily heavy metal ions such as Ni^{2+}, Cu$^+$, Hg^{2+}, Ag$^+$ and Cd^{2+} is well recognized and has led to the preparation and structural characterization of a large number of such compounds and their metal complexes.[1–7] From the structural data accumulated thus far, it has become evident that preorganization of the ligand is

quite important and to a large extent may determine the mode of complexation of these heavy metal ions.[8–10] In particular those macrocyclic thioethers that contain ethylene bridges between the sulfur atoms usually adopt an overall anti-type conformation in which the sulfur ligating sites point away from the molecular cavity. This frequently leads to the formation of metal complexes with fractional stoichiometries with respect to the ligand.[11] The introduction of functional groups suitable for further functionalization offers, at least in principle, the possibility of other strategies for manipulation of conformation of the macrocycle as well as for adaptation of the molecular properties. For example, the introduction of alkylidene or keto groups (eq 1) opens a route

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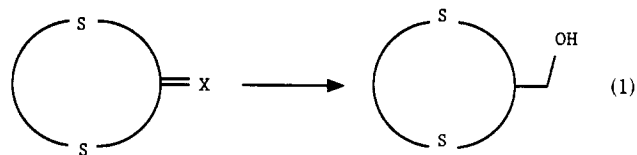
to hydroxyl substituted macrocyclic derivatives that might exhibit, among other things, water solubility. In the case of carbonyl functionalized derivatives we envisage further functionalization

[†] Department of Organic and Molecular Inorganic Chemistry, University of Groningen.

[‡] Molecular Structure Center, University of Groningen.

[§] University of Utrecht.

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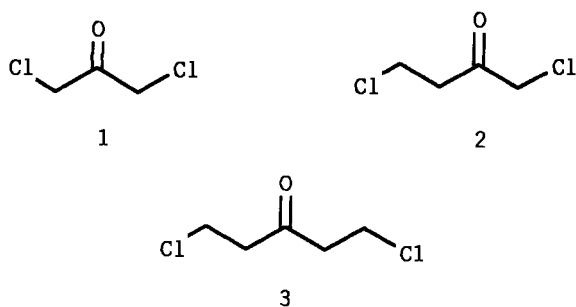
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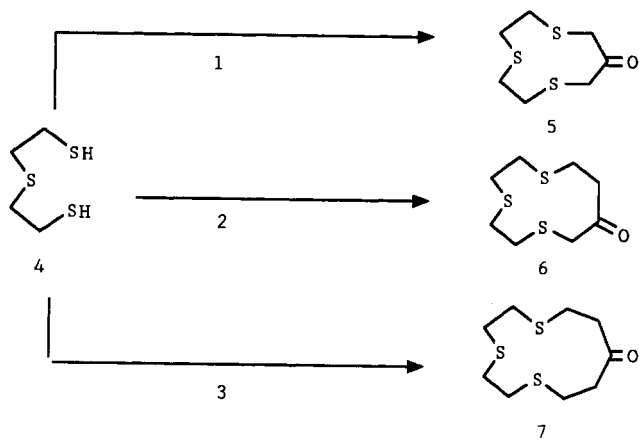
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Chart 1

Scheme 1

Figure 1. Perspective drawing of **5**. Selected bond angles (deg) and distances (Å): S(5)–C(6)–C(7)–S(8) = 63.74(3), S(8)–C(9)–C(10)–S(1) = 58.18(2), S(1)–C(2)–C(3)–O(1) = 136.21(6), C(2)–C(3)–O(1) = 119.9(2); O(1)–C(1) = 1.208(3).

via, for example, Wittig, Grignard, or aldol type chemistry. We now report a straightforward synthesis and structural characterization of novel cyclic thiocrown ethers in which the different alkanone building blocks **1–3** (Chart 1) are incorporated. The application of 1,3-dichloroacetone (**1**) in the synthesis of keto thiocrown ethers has been described in a preliminary report.[9a]

Results and Discussion

The general synthetic pathway to the three cyclic thioethers is illustrated in eq 2. The key step, developed in our laboratory, is the cesium-based ring closure of an α,ω-dihalide with a particular dithiol.[12–14] Via compounds **1–3**, it is possible to vary selectively

$$(2)$$
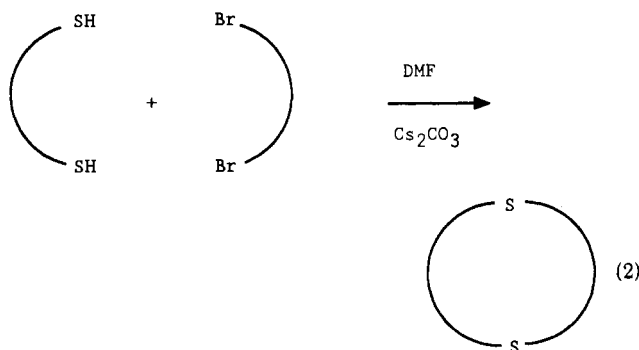
the ring size and the flexibility of the thiocrown ether. Cyclization of 3-thiapentane-1,5-dithiol(**4**) as the cesium dithiolate with **1**, **2** and **3** affords in good yield the corresponding macrocycles **5**, **6** and **7** (Scheme 1). Compound **5** has recently been reported by Setzer and Grant.[15] Optimum yields for **5** were obtained when

Figure 2. Thermal motion ellipsoid (50% probability) plot of **6**. Selected bond angles (deg) and distances (Å): S(1)–C(3)–C(4)–S(2) = –60.0(5), S(2)–C(5)–C(6)–S(3) = –68.9(5), S(1)–C(2)–C(1)–O(1) = –133.2(6); O(1)–C(1) = 1.207(8).

the reactions were carried out on a 10^{-2} M scale at roughly 50 °C in DMF/THF mixtures. For the preparation of the nonsymmetric keto crown ether **6**, it proved necessary to keep strict control of the reaction temperature. Optimum yields were obtained by performing this reaction at 40–45 °C in neat THF with K_2CO_3 rather than Cs_2CO_3 as base. The molecular structure of **5**, as determined by X-ray crystallography, shows that the molecule adopts a crown-like conformation in the solid state (Figure 1). The rigidity induced by the keto fragment causes a slight deviation from the ideal crown structure found in the C_3-symmetrical 9-S-3 and its metal derivatives.[5a,16–18] The carbonyl moiety points away from the molecular cavity, thereby tilting S3 out of the idealized S3 plane. As a result two sulfur atoms and the carbonyl oxygen atom adopt a crown-type arrangement. The molecular structures of **6** and **7** are shown in Figures 2 and 3, respectively. Molecule **7** adopts a more open structure with larger S–C–C–S torsion angles (for **7** S(1)–C(4)–(5)–S(2) = –179.6(7)°) than both **5** and **6**, which attain a nearly all-gauche orientation for the sulfur atoms (for **6** S(1)–C(3)–C(4)–S(2) = –60.0(5)° and S(2)–C(5)–C(6)–S(3) = –68.9(5)°). This conformational arrangement of **7** is probably a result of both an increased flexibility of the pentanone fragment and the larger

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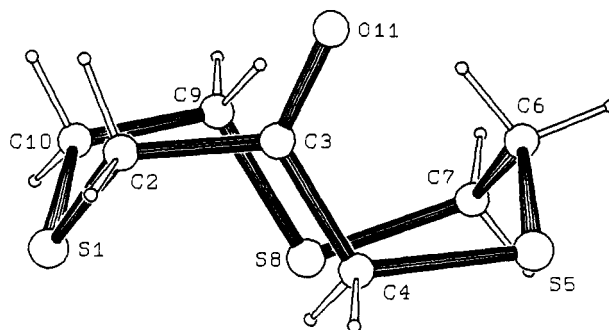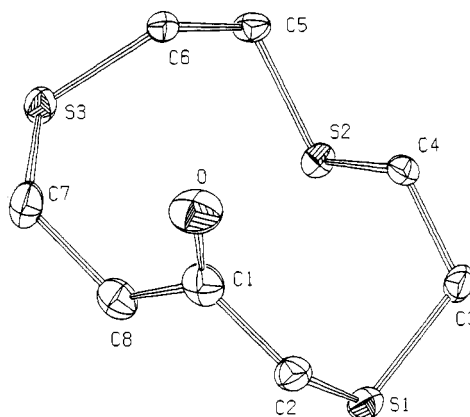
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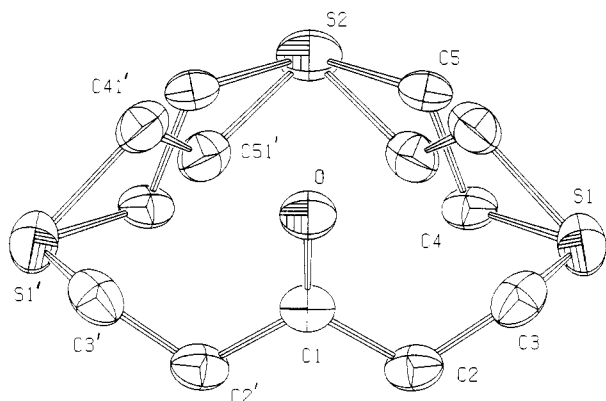
Figure 3. Thermal motion ellipsoid plot (50% probability) of **7**. (The two conformers due to disorder in the ring are shown.) Selected bond angles (deg) and distances (Å): S(1)–C(4)–C(5)–S(2) = –179.6(7), C(1)–C(2)–C(3)–S(1) = –101.1(5), C(2)–C(1)–O(1) = 120.6(3); O(1)–C(1) = 1.226(9).

Table 1. Crystal Data and Structural Analysis Results

	5	**6**	**7**
formula	C$_7$H$_{12}$OS$_3$	C$_8$H$_{14}$OS$_3$	C$_9$H$_{16}$OS$_3$
MW	208.37	222.40	236.42
space group	*P*2$_1$	*P*1̄	*Pnma*
cryst syst	monoclinic	triclinic	orthorhombic
Z	2	2	4
a (Å)	7.145(1)	5.408(4)	15.4077(3)
b (Å)	5.310(1)	7.366(3)	15.3536(17)
c (Å)	11.932(1)	13.581(4)	4.9889(11)
α (deg)		80.87(3)	
β (deg)	96.57(1)	78.68(5)	
γ (deg)		69.79(5)	
V (Å^3)	449.7(1)	495.4(5)	1180.2(3)
D$_{calc}$ (g cm^{-3})	1.539	1.491	1.331
μ (cm^{-1})	7.34	6.7	5.7
radiation (Mo Kα (Å))	0.710 73	0.710 73	0.710 73
T (K)	130	100	298
R^a	0.024	0.074	0.072
R$_w$^{b}	0.032	0.095	0.080

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

Table 2. Bond Distances (Å) for **5**^{a}

S(1)–C(2)	1.812(2)	S(5)–C(4)	1.811(2)
S(1)–C(10)	1.817(3)	S(5)–C(6)	1.816(3)
S(8)–C(7)	1.816(2)	O(11)–C(3)	1.208(3)
S(8)–C(9)	1.815(3)	C(2)–C(3)	1.523(3)
C(3)–C(4)	1.512(4)	C(9)–C(10)	1.528(3)
C(6)–C(7)	1.529(3)		

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3. Positional Parameters and Their Estimated Standard Deviations for **5**

atom	*x*	*y*	*z*	*b* (Å2)
S(1)	0.49536(7)	0.300	0.89394(5)	1.186(8)
S(5)	1.01875(8)	0.0074(1)	0.70500(5)	1.368(9)
S(8)	0.55204(8)	0.2531(1)	0.61520(5)	1.148(8)
O(11)	1.0213(2)	0.4393(4)	0.8768(2)	1.51(3)
C(2)	0.7364(3)	0.3558(5)	0.9538(2)	1.25(4)
C(3)	0.8919(3)	0.2943(5)	0.8809(2)	1.02(3)
C(4)	0.8772(3)	0.0436(5)	0.8206(2)	1.20(3)
C(6)	0.9508(3)	0.2736(5)	0.6139(2)	1.30(3)
C(7)	0.7603(3)	0.2631(6)	0.5411(2)	1.40(4)
C(9)	0.5780(3)	0.5459(5)	0.6940(2)	1.15(3)
C(10)	0.4547(3)	0.5510(5)	0.7905(2)	1.24(4)

size of the ring system. Crystal data and structural analysis results for **5–7** are given in Table 1 and bond distances, bond angles, and positional parameters for **5–7** are given in Tables 2–7. Compound **6** is to our knowledge the first example of a nonsymmetrical carbonyl functionalized thiocrown ether. The

Table 4. Bond Distances (Å) and Angles (deg) for **6**

S(1)–C(2)	1.817(6)	O–C(1)	1.207(8)
S(1)–C(3)	1.818(7)	C(1)–C(2)	1.515(9)
S(2)–C(4)	1.808(6)	C(1)–C(8)	1.498(10)
S(2)–C(5)	1.805(6)	C(3)–C(4)	1.518(8)
S(3)–C(6)	1.810(7)	C(5)–C(6)	1.530(7)
S(3)–C(7)	1.815(6)	C(7)–C(8)	1.570(8)
C(2)–S(1)–C(3)	101.4(3)	S(1)–C(3)–C(4)	116.1(4)
C(4)–S(2)–C(5)	100.1(3)	S(2)–C(4)–C(3)	113.2(4)
C(6)–S(3)–C(7)	102.8(3)	S(2)–C(5)–C(6)	115.4(4)
O–C(1)–C(2)	123.6(6)	S(3)–C(6)–C(5)	112.2(4)
O–C(1)–C(8)	121.6(6)	S(3)–C(7)–C(8)	113.1(4)
C(2)–C(1)–C(8)	114.6(6)	C(1)–C(8)–C(7)	113.0(5)
S(1)–C(2)–C(1)	118.3(4)		

Table 5. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for **6**

atom	*x*	*y*	*z*	*U*(eq) (Å^2)^a
S(1)	0.1261(3)	0.1505(2)	0.04791(10)	0.0192(4)
S(2)	–0.1075(3)	0.052015(19)	0.20379(10)	0.0166(4)
S(3)	–0.4223(3)	0.2973(2)	0.41662(10)	0.0196(4)
O	0.2486(9)	–0.1005(6)	0.3156(3)	0.0334(14)
C(1)	0.1169(13)	–0.0449(8)	0.2479(5)	0.0251(19)
C(2)	0.2340(12)	–0.0612(8)	0.1375(4)	0.0211(17)
C(3)	0.3098(12)	0.3002(8)	0.0718(4)	0.0200(17)
C(4)	0.2378(11)	0.3720(7)	0.1758(4)	0.0152(17)
C(5)	–0.1270(12)	0.5431(7)	0.3357(4)	0.0181(14)
C(6)	–0.1218(11)	0.3593(7)	0.4070(4)	0.0168(16)
C(7)	–0.2944(13)	0.0489(8)	0.3834(4)	0.0269(19)
C(8)	–0.1813(12)	0.0334(8)	0.2683(4)	0.0239(17)

^{a} *U*(eq) = $^1/_3$ of the trace of the orthogonalized **U**.

Table 6. Bond Distances (Å) and Angles (deg) for **7**

S(1)–C(3)	1.801(5)	O–C(1)	1.226(9)
S(1)–C(4)	1.810(6)	C(1)–C(2)	1.490(6)
S(1)–C(41)	1.91(3)	C(2)–C(3)	1.507(7)
S(2)–C(5)	1.872(16)	C(4)–C(5)	1.53(2)
S(2)–C(51)′	1.80(3)	C(41)′–C(51)′	1.45(3)
C(3)–S(1)–C(4)	107.4(5)	C(1)–C(2)–C(3)	115.8(4)
C(3)–S(1)–C(41)	96.7(8)	S(1)–C(3)–C(2)	116.6(4)
C(5)–S(2)–C(51)′	102.0(9)	S(2)–C(5)–C(4)	109.0(10)
S(1)–C(4)–C(5)	109.4(9)	S(2)–C(51)′–C(41)′	113.7(17)
O–C(1)–C(2)	120.6(30)	S(1)′–C(41)′–C(51)′	107.8(16)
C(2)–C(1)–C(2)′	118.7(6)		

Table 7. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for **7**

atom	*x*	*y*	*z*	*U*(eq) (Å^2)^a
S(1)	0.14156(10)	0.03632(9)	0.0293(4)	0.0881(7)
S(2)	0.33131(13)	$^1/_4$	–0.0831(5)	0.0796(9)
O	0.0901(4)	$^1/_4$	0.4351(11)	0.080(2)
C(1)	0.0451(4)	$^1/_4$	0.2325(16)	0.057(3)
C(2)	0.0153(3)	0.01665(3)	0.1111(11)	0.0643(19)
C(3)	0.0558(3)	0.0850(3)	0.2236(11)	0.073(2)
C(4)*	0.2025(10)	0.1239(11)	–0.124(2)	0.058(4)
C(5)*	0.2693(10)	0.1590(11)	0.077(3)	0.066(5)
C(41)*	0.2290(18)	0.1204(16)	0.115(4)	0.074(8)
C(51)*	0.2486(18)	0.1688(16)	–0.127(4)	0.070(8)

^{a} *U*(eq) = $^1/_3$ of the trace of the orthogonalized **U**. Starred atom sites have a population less than 1.0.

chemistry of the above mentioned thiocrown ethers is currently under investigation. Preliminary results from condensation reactions with amines and hydrazines demonstrate the reactivity of the implemented keto fragments.[9b] Conductometric titrations of AgOTf in MeCN and THF with crowns **5–7** clearly demonstrate the important role of the solvent in complex formation.[19] In Figure 4, the titration of AgOTf in MeCN is shown. With ligand **5**, complex formation is evident but the stoichiometry of the complex is not clear. With **7**, an abrupt

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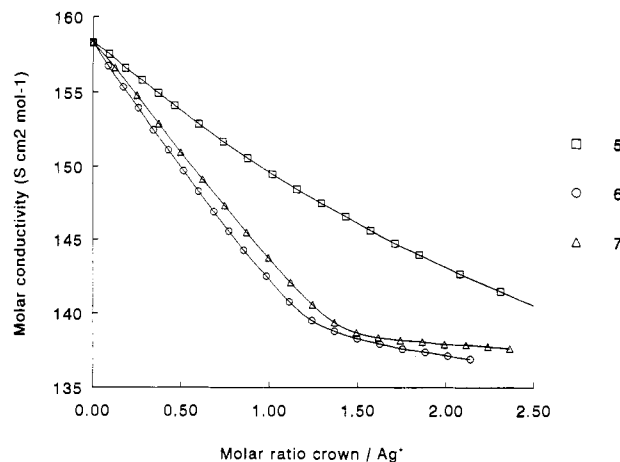
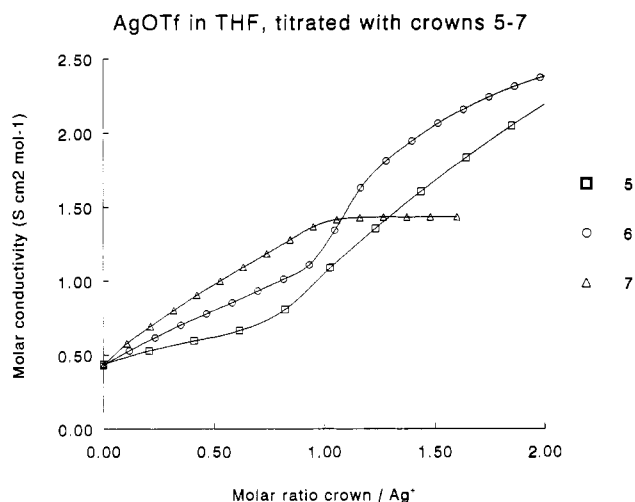**Figure 4.** Plot of the molar conductivity versus ratio (L)/AgO₃SCF₃ (in MeCN): L = **5** (□), **6** (O), and **7** (△).

Figure 5. Plot of the molar conductivity versus ratio (L)/AgO₃SCF₃ (in THF): L = **5** (□), **6** (O), and **7** (△).

change in slope is observed at molar ratio L/Ag⁺X⁻ = 1.5, which indicates the formation of a complex having Ag₂(CF₃SO₃)₂L₃ stoichiometry, which is partially ionized in solution. For **6**, the break in the titration curve lies between 1 and 1.5. The sharp drop in the conductivity, observed for AgO₃SCF₃ within the range (L)/Ag⁺ = 0.0–1.5 (Figure 4) indicates a strong complexation of **6** and **7** with Ag⁺ in MeCN. This efficient complexation of **6** and **7** is most certainly a result of the favorable steric requirements and the increased flexibility of the ligand system resembling the open-chain analogs. In the case of the more rigid ligand **5**, the more shallow curve may be caused by a less efficient competition with MeCN as coordinating ligand.[20] Different results are obtained when THF is the solvent (Figure 5). Again, no conclusions can be drawn concerning the stoichiometry of the AgOTf complex with **5**. Ligand **6** shows quite interesting behavior. Up to molar ratio L/Ag⁺X⁻ = 1.0 the 1:1 adduct is formed. Beyond this point, another—more difficult to identify—stoichiometry is favoured. With **7** only the 1:1 adduct is formed. In THF an increase in molar conductivity is observed. This is a consequence of the fact that in THF AgOTf is not (completely) dissociated into ions. Addition of crown ether results in complex formation with the metal center and forces the ion-pairs to separate, thus increasing the conductivity.

Complexation of **5** with AgOTf in MeCN resulted in the formation of the 1:1 adduct. A preliminary X-ray diffraction study of AgO₃SCF₃·**5** revealed the molecular structure of the
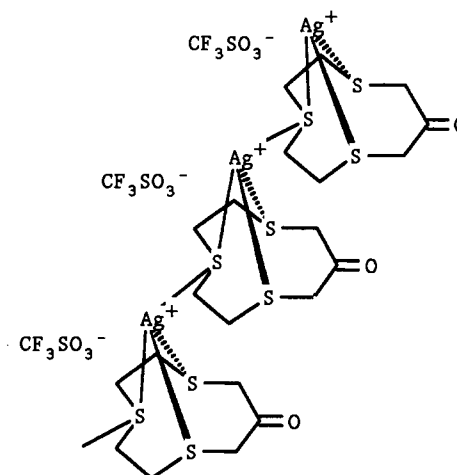
Figure 6. Schematic representation of polymeric unit thought to be present in [AgO₃SCF₃·**5**]ₙ.

complex to consist of polymeric helical strings with bridging thiocrown ethers between the individual Ag⁺ ions (Figure 6).[21] The coordination sphere of Ag⁺ is constituted by a facially capping crown ether, whereas the residual site is occupied by a sulfur atom of a neighboring Ag⁺ (L) unit. Due to heavy disorder problems an accurate solution of the structure is not yet possible, although the general aspects of the structure of AgO₃SCF₃·**5** are clear. The ¹H-NMR spectrum of the complex shows slightly shifted signals due to the coordination of Ag⁺. The characteristic absorptions at 2.87 (CH₂–S) and 3.65 (CH₂–C(O)) ppm (singlets) are shifted and split into absorptions at 2.82, 2.96, 3.03 and 3.45 ppm (broad singlets), respectively, suggesting asymmetric coordination in solution. This indication is reinforced by the ¹³C-NMR data that show seven independent signals for coordinated **5**.

Summary

The crystal structures of three different thiocrown ethers containing keto groups are now available. It is clear that all three ligands (**5**–**7**) complex with Ag⁺ in solution. In both MeCN and THF ligand **7** leads to discrete stoichiometries whereas for **5** and **6** this is not always the case. Clearly further investigation is required to establish the identities of the various complexes and to define adequately the relation between thiocrown ether structure and complexation behavior.

Experimental Procedure

Aldrich supplied 1,3-dichloroacetone and 3-thiapentane-1,5-dithiol, and these were used as received. Dihalides **2** and **3** were prepared according to literature procedures by reaction of the acid halide with gaseous ethylene under Friedel–Crafts conditions with AlCl₃.[22]

¹H-NMR and ¹³C-NMR spectra were recorded on a Varian 200 MHz spectrometer. Infrared data were obtained from a Perkin-Elmer 781 spectrometer. Mass spectra were recorded on a AEI-MS9 mass spectrometer. Conductometric experiments were performed in HPLC-UV grade MeCN (Janssen Chimica) and THF—distilled from Na/benzophenone (Janssen Chimica)—according to literature methods with a Philips platinum electrode PW 9512/01 and a Wayne Kerr Autobalance B642 universal bridge.[19]

Preparation of 3,6,9-Trithiacyclodecanone (5). A solution of 3-thia-pentane-1,5-dithiol (**4**) and **1** in DMF both 1.8 mmol/L, was added dropwise to a stirred suspension of Cs₂CO₃ (2.2 mmol/L) in dry DMF at 55 °C over a period of 10–16 h. After addition, the stirring was continued for 4 h. The mixture was filtered to remove the unreacted Cs₂CO₃ and CsCl. The solvent was removed in vacuo, and the residual solid was chromatographed over silica gel using CH₂Cl₂/hexane 2:1 as

(20) (a) Janz, G. J.; James, D. W. *J. Chem. Phys.* **1961**, *33*, 739. (b) Baddiel, C. B.; Tait, M. J.; Janz, G. J. *J. Phys. Chem.* **1965**, *69*, 3634.

(21) The X-ray data are not of sufficient quality to justify publication of the structure in detail at this moment. Remeasurements of the data set are ongoing, and the results will be dealt with in a forthcoming paper.

(22) Owen, G. R.; Reese, C. B. *J. Chem. Soc. C* **1970**, 2401.

eluent. The organic layer was evaporated leaving a creamy-white solid, yield 72%. ^{1}H-NMR (CDCl$_3$): δ 2.87 (s), 3.65 (s). ^{13}C-NMR (CDCl$_3$): δ 32.01 (t), 32.95 (t), 40.95 (t), 202.32 (s). IR (KBr, cm^{-1}): 2950 m, 1710 s, 1650 s, 1400 s, 1280 s, 1210 m, 1080 s, 920 w. HRMS (m/e): 208.031 (theoretical for C$_7$H$_{12}$O$_3$S 208.032).

Preparation of 3,6,9-Trithiacycloundecanone (6). A solution of **4** and **2** in THF, both 1.8 mmol/L, was added dropwise to a stirred suspension of Cs$_2$CO$_3$ (2.2 mmol/L) in dry THF/DMF (10:1) at 55 °C over a period of 10–16 h. After addition, the stirring was continued for 6 h. The mixture was filtered to remove the unreacted Cs$_2$CO$_3$ and CsCl. The solvent was removed in vacuo and the residual solid was chromatographed over silica gel using CH$_2$Cl$_2$/hexane 2:1 as eluent. The organic layer was evaporated leaving a creamy-white solid, yield 52%. ^{1}H-NMR (CDCl$_3$): δ 2.87 (m), 2.94 (m), 3.18 (m (AB system)), 3.20 (s). ^{13}C-NMR-(CDCl$_3$): δ 25.96 (t), 31.04 (t), 32.92 (t), 33.60 (t), 34.99 (t), 41.63 (t), 43.11 (t), 202.01 (s). IR (KBr, cm^{-1}): 2917 m, 1695 s, 1450 m, 1410 s, 1393 s, 1370 s, 1358 s, 1270 s, 1259 m, 1220 m, 1207 s, 1181 m, 1148 m, 1117 m, 1091 s, 944 s, 895 s, 861 m. HRMS (m/e): 222.020 (theoretical for C$_8$H$_{14}$O$_3$S 222.021).

Prepration of 4,7,10-Trithiacyclododecanone (7). A solution of **4** and **3** in DMF, both 1.8 mmol/L, was added dropwise to a stirred suspension of Cs$_2$CO$_3$ (2.2 mmol/L) in dry DMF at 45 °C over a period of 10–16 h. After addition the stirring was continued for 4 h. The mixture was filtered to remove the unreacted Cs$_2$CO$_3$ and CsCl. The solvent was removed in vacuo, and the residual solid was chromatographed over silica gel using CH$_2$Cl$_2$/hexane 2:1 as eluent. The organic layer was evaporated leaving a white solid, yield 63%. ^{1}H-NMR (CDCl$_3$): δ 2.75 (m), 3.87 (m). ^{13}C-NMR (CDCl$_3$): δ 24.15 (t), 31.85 (t), 33.14 (t), 44.22 (t), 207.91 (s). IR (KBr, cm^{-1}): 2961 s, 1700 s, 1683 s, 1424 s, 1400 s, 1363 s, 1276 s, 1263 s, 1214 m, 1196 s, 1132 s, 1120 s, 1076 s, 1040 m, 975 s, 955 s, 925 mw. HRMS (m/e): 236.036 (calcd 236.036 for C$_9$H$_{16}$O$_3$S).

Crystal Structure Determination (General). Crystal data and details on refinements are presented in Table 1. X-ray data for **5** were collected on an Enraf-Nonius CAD4F diffractometer interfaced with a VAX-730 computer. X-ray data for **6** and **7** were collected on an Enraf-Nonius CAD4T diffractometer on a rotating anode. Calculations were performed on a DEC5000 system. Scattering factors were taken from Cromer and Mann and have been corrected for anomalous dispersion (Cromer and Liberman).[23,24]

Crystal Structure Determination of C$_7$H$_{12}$O$_3$S (5). A colorless crystal of approximate dimensions 0.30 × 0.25 × 0.20 mm was used for the data collection. Accurate unit cell parameters and orientation matrix were obtained by least-squares refinement of 25 well-centered reflections in the range 10.4° < θ < 21.8°. On the basis of systematic absences, the space group was determined to be $P2_1$. The data collection was performed at 130 K with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation using the θ–2θ scan technique. From a total of 1644 reflections (I > 3σ(I)) in the range 1° < θ < 27°, 1640 were used in the refinements. Scaling factors based on the fluctuations of the standard reflections and Lorentz, polarization, and absorption corrections (minimum and maximum transmission 74.55% and 89.63% respectively) were applied to the data. The structure was solved by direct methods and the remaining H atoms were located from a difference Fourier map based on the non-H atoms. The structure was refined with full-matrix least-squares techniques to R = 0.024 and R_w = 0.032 including 130 parameters.

Structure Determination of C$_8$H$_{14}$O$_3$S (6). A total of 4990 reflections were scanned ($\omega/2\theta$ scan, $\Delta\omega$ = 0.73 + 0.35 tan θ°, θ_{max} = 27.5°, T = 100 K) for a colorless transparant plate-shaped crystal glued on a glass fiber. Unit cell parameters were derived from the SET4 setting angles of 25 reflections (10° < θ < 14°). Data were corrected for Lp and absorption/extinction (DIFABS; correction range 0.85:1.33).[25] The structure was solved with DIRDIF92 and refined on F by full-matrix least-squares techniques with SHELX76 to R = 0.074 (R_w = 0.095, w^{-1} = $\sigma^2(F)$) for 2104 observed reflections with I > 3.0σ(I) and 110 parameters.[26,27] The calculations of geometrical data and the illustrations were done with PLATON-92.[28]

Structure Determination of C$_9$H$_{16}$O$_3$S (7). A total of 3229 reflections were scanned ($\omega/2\theta$ scan, $\Delta\omega$ = 0.97 + 0.35 tan θ° θ_{max} = 27.5°, T = 298 K) for a colorless crystal glued on a glass fiber. Unit cell parameters were derived from the SET4 setting angles of 25 reflections (10° < θ < 14°). Data were corrected for Lp and absorption/extinction (DIFABS; correction range 0.55:1.53).[25] The structure was solved with DIRDIF92 and refined on F by full-matrix least-squares techniques with SHELX 76.[26,27] A disorder model (59:41) was used to describe the observed conformational disorder of the ring puckering. Hydrogen atoms were taken into account at calculated positions. Convergence was reached at R = 0.072 (R_w = 0.080, w^{-1} = $\sigma^2(F)$ + 0.000045F^2) for 740 observed reflections with I > 2.5σ(I) and 84 parameters.

Conductometric Measurements. In order to obtain information about the stoichiometry of the complexes in solution, the following procedures were used: a AgO$_3$SCF$_3$ solution in MeCN (1.02 × 10^{-3} M) or THF (0.992 × 10^{-3} M) was titrated with a solution of **5**, **6**, or **7** in the same solvent. Conductivities were measured at fixed temperature (25.0(1) °C), and the corresponding molar conductivities were computed. If complexation were restricted to certain discrete stoichiometries, an abrupt change of slope in the conductivity plot is to be expected.

Supplementary Material Available: Text detailing the structure solution, tables of bond distances, bond angles, rms amplitudes, least-squares planes, torsional angles, anisotropic thermal parameters, and complete positional parameters, and two views of the structure for **5** and tables of crystal data, positional and isotropic thermal parameters of non-hydrogen atoms, anisotropic thermal parameters of non-hydrogen atoms, positional parameters and isotropic thermal parameters of hydrogen atoms, bond distances, bond angles, and torsional angles for **6** and **7** (21 pages). Ordering information is given on any current masthead page.

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