Silver(I) Complexes of the Derivatized Crown Thioether Ligands 3,6,9,12,15,18-Hexathianonadecanol and 3,6,9,13,16,19-Hexathiaicosanol. Determination of Stability Constants and the Crystal Structures of [Ag(19-aneS6-OH)][CF_3SO_3] and [Ag(20-aneS6-OH)][BF_4]

Roger Alberto,[†] Walter Nef,[†] Alan Smith,[†] Thomas A. Kaden,[‡] Markus Neuburger,[‡] Margareta Zehnder,[‡] Alfred Frey,[§] Ulrich Abram,[||] and P. August Schubiger*,[†]

Division of Radiopharmacy, Paul Scherrer Insitute, CH-5232 Villigen, Switzerland, Institute of Inorganic Chemistry, University of Basel, CH-4056 Basel, Switzerland, AC-Laboratory, AC-Zentrum, CH-3700 Spiez/Switzerland, and Institute of Inorganic Chemistry, University of Tübingen, D-72076 Tübingen, Germany

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The derivatized 19- and 20-membered macrocyclic thio crowns 3,6,9,12,15,18-hexathianonadecanol $C_{13}H_{26}OS_6$ (19-aneS6-OH) (**1**) and 3,6,9,13,16,19-hexathiacycloicosanol $C_{14}H_{28}OS_6$ (20-aneS6-OH) (**2**) have been synthesized by [1 + 1] cyclization in about 30% yield. The ligands **1** and **2** react readily at room temperature with different silver(I) salts in water and in organic solvents to form in quantitative yields the complexes [Ag(19-aneS6-OH)]$^+$ (**3**) and [Ag(20-aneS6-OH)]$^+$ (**4**) for which crystals of X-ray quality were grown by slow diffusion of diethylether into methanol. [Ag(19-aneS6-OH)][CF_3SO_3] crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, $a = 10.760(1)$, $b = 10.853(2)$ and $c = 11.326(2)$Å, and $\alpha = 78.73(1)$, $\beta = 73.47(1)$, and $\gamma = 74.99(1)$°. [Ag(20-aneS6-OH)][BF_4] also crystallizes in the triclinic space group $P\bar{1}$ with $Z = 4$. The unit cell constants were determined with $a = 10.076(4)$, $b = 10.525(3)$, and $c = 22.135(8)$Å, $\alpha = 93.32(2)$, $\beta = 102.43(2)$, and $\gamma = 100.32(2)$°. The complex cations [Ag(19-aneS6-OH)]$^+$ and [Ag(20-aneS6-OH)]$^+$ are coordinated through only four sulfur atoms; thus, a distorted tetrahedral coordination geometry is exhibited. In addition we found a highly asymmetric Ag−S bond lengths distribution throughout all complex cations. The stability constants of [Ag]$^+$ with **1** and **2** and, for comparison with [18-aneS6] (**5**), have been determined in methanol by potentiometric [Ag]$^+$ measurements. Log *K* values for the formation of **3**, **4**, and [Ag(18-aneS6]$^+$ (**6**) are 12.04 ± 0.19, 11.49 ± 0.15, and 12.67 ± 0.13 respectively. Owing to a comparable macrocyclic effect, the similar log *K* values are reasonable but, since **6** coordinates octahedrally, not expected. ^{1}H and ^{13}C NMR investigations at various temperatures give evidence for fluxional coordinative behavior between all six sulfur atoms in solution. Consequently [Ag(19-aneS6-OH)]$^+$, [Ag(20-aneS6-OH)]$^+$, and [Ag(18-aneS6]$^+$ seem to exhibit principally the same solution structures although the solid structures are very different.

Introduction

The coordination chemistry of macrocyclic thio crown ligands is an intensive area of study and several relevant reviews in the recent past have demonstrated impressively the usefulness of this ligand type in basic research as well as in practice orientated fields.[1−4] Complexes of macrocyclic thio crowns with differing ring size and number of sulfur atoms for coordination with a variety of metal centers have been published.[5−11] The most broad studies have been performed with [9-aneS3] (**7**) or [18-aneS6] (**5**), whereas investigations on higher- or odd-membered rings have been less frequent. We are particularly interested in potentially hexadentate thio crowns because they are expected to form stable and inert complexes with silver(I). To our knowledge only the complexes [Ag(18-aneS6)]$^+$ (**6**) and [Ag-(16-aneS6)]$^+$ (**8**) see Chart 1 have been described in detail and structurally characterized.[12−13] The former exhibits an octahedral coordination geometry while the latter has a coordination number of four with distorted tetrahedral geometry.

Silver(I) complexes are interesting because the isotope ^{111}Ag has been proposed for application in radioimmunotherapy due to its very favorable decay properties such as medium half-life, convenient β-energy, and low percentage of accompanying γ-emission.[14−16] To allow defined application of this nuclide in protein labeling techniques for nuclear medical purposes, a

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* Corresponding author.

[†] Paul Scherrer Institute.

[‡] University of Basel.

[§] AC-Zentrum.

[||] University of Tübingen.

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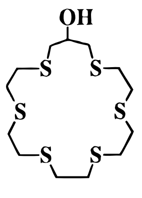
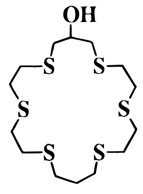
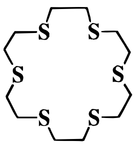
Chart 1



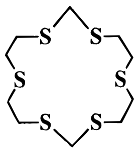
[19-aneS6-OH]



[20-aneS6-OH]



[18-aneS6]



[16-aneS6]

potential ligand must stabilize the Ag(I) center under *in vivo* conditions for days. It has been stated by several authors that the kinetic stability of such metal complexes is as important as thermodynamic stability.[17,18] A systematic study of Ag(I) complexes in general reveals that log *K* values rarely exceed about 13 for mononuclear complexes.[19] Typical stability constants with tetradentate thio crowns in methanol are usually in the range 7−8,[20] with those with [N2S2] macrocycles of variable ring size, determined in water, between 7 and 11,[21] whereas the highest values described to our knowledge are those with macrocyclic $[N_xS_y]$ systems ($x + y = 6$), where values of about 14 for [18-aneN2S4][22] were achieved. In the case of Ag(I), stability constants are usually higher with ligands containing nitrogen instead of sulfur, but since pH equilibria are involved for amine nitrogens much lower stabilities under physiological conditions are expected.[23] Some typical values are shown in Table 6.

Silver(I) is known to be a very labile metal center, and ligand exchange processes usually occur very fast. Only ligands, such as thio crowns, able to encapsulate the $[Ag]^+$ center might provide increased kinetic stability to prevent the $[Ag]^+$ center from fast trans-metalation processes to other competing coordination sites occuring frequently in biological systems. Thio crowns are not involved in pH equilibria which would decrease the thermodynamic stability. Thermodynamic data of thio crowns are not very numerous. We determined the stability constants for the complexation of **1**, **2**, and **5** with Ag(I).

The hydroxyl group at the C-backbone in **1** and **2** has been chosen because it is not expected to compete in coordination and is easily transformed to amines or other substituents with linking potential.

Experimental Section

Materials. 3,6-Dithia-1,8-octandiol (**10**) was purchased from Merck AG Darmstad, Germany; all other chemicals have been purchased from Fluka AG, Buchs, Switzerland, and used without further purification. Solvents, especially DMF were carefully dried by common methods before using.[24] *Caution*! Chlorination of the diols **10** and **12** yields mustard gas derivatives. Especially **11**, known as "Q-Yperite" is an extremly harmful vesicant. The synthesis and handling of these compounds should only be performed in specialized laboratories equipped with well-ventilated hoods.

Measurements. Fourier transformed *infrared* spectra were obtained on a Perkin-Elmer 16PC spectrophotometer. NMR experiments were performed on a Varian Gemini 2000 300-MHz system using CD_3CN, $CDCl_3$, or CD_3OD as solvent and as internal reference. Mass spectra were recorded on a Fisons VG Trio 2000 mass spectrometer by electrospray ionization. Potentiometric measurements were performed in carefully purified and dried methanol. For the measurements, a Ag electrode with an internal Ag/AgCl reference electrode and a saturated LiCl/ethanol bridge was used. Before every measurement, E_o and *s* of the chain were determined with stock solutions of well-defined concentration. For the determination of the stability constants, the ligand was dissolved in methanol and $[Ag]^+$ (solution of $[Ag][ClO_4]$ in methanol) added by a buret. Typical concentrations of the ligand and $[Ag]^+$ were in the range of 10^{-3} M. The concentration of $[Ag]^+$ was determined prior to every measurement with a standard $[Cl]^-$ solution. $[Ag]^+$ solutions were stored in the dark at low temperatures. All solutions were maintained at 0.1 M ionic strength with $[NBu_4][ClO_4]$.

Preparation of 1,9-Mercapto-3,7-dithia-5-nonanol (9). Sodium (4.65 g, 202.1 mmol) was dissolved in 60 mL of dry ethanol. The solvent was removed *in vacuo*, ethanedithiol (87.04 g, 924.0 mmol) added to the white residue and diluted with ethanol till the solution turned clear. The solution was refluxed and 1,3-dichloro-2-propanol (11.90 g, 92.4 mmol) added dropwise over a period of 2 h. Heating was continued for another 30 min and insoluble NaCl removed by filtration. Removing of the solvent *in vacuo* and subsequent purification of the oily residue by column chromatography on silica gel using ethyl acetate/hexane 2:3 as eluent gave the product in the first fraction as a colorless oil (14.20 g, 63%). IR (cm^{-1}, KBr pellet): 3446 (s), 2914 (s), 2546 (m), 1422 (s) cm^{-1}. ^1H NMR (in $CDCl_3$, δ): 3.83 (q, 1H), 2.96 (s, 1H,), 2.5−2.9 (m, 12H), 1.75 (m, 2H). Anal. Calcd for $C_7H_{16}OS_4$: C, 34.39; H, 6.60. Found: C, 35.03, H, 6.74.

Preparation of 3,6-Dithia-1,8-dichlorooctane (11). (*Caution*! The product is a very harmful, blister-causing mustard compound). 3,6-Dithia-1,8-octanediol (12 g, 65,8 mmol) was dissolved in 80 mL of dry THF. Thionyl chloride (17.2 g, 144.6 mmol) was slowly added and the generated HCl and SO_2 were removed into a flask filled with saturated NaOH solution. The mixture was stirred for 1 h and then treated with a saturated solution of $NaHCO_3$ until neutralized. The organic layer was separated and the water layer treated with another 50 mL of $CHCl_3$. The combined organic extracts were dried over Na_2SO_4. $CHCl_3$ was evaporated *in vacuo* to obtain a solid residue, which was recrystallized with *tert*-butanol to yield **11** as a white crystalline solid (10.96 g, 76%): IR (cm^{-1}, KBr pellet): 2964 (m), 2930 (m), 1436 (s), 1420 (m), 1306 (m), 1230 (m), 1198 (s), 1138 (m), 1042 (w), 694 (s), 758 (w), 702 (s), 676 (s) cm^{-1}. ^1H NMR (in $CDCl_3$, δ): 3.64 (t, 4H), 2.88 (t, 4H), 2.78 (s, 4H). ^{13}C NMR (δ, $CDCl_3$): 43.68, 34.96, 33.12. MS (*m*/*e*): 219 (theoretical for $C_7H_{16}S_2O_2$ 219.2).

Preparation of 3,7-Dithia-1,9-nonanediol (12). Sodium (6.72 g, 292 mmol) was dissolved in 120 mL of dry ethanol. 1,3-Propandithiol (15.60 g, 144.2 mmol) was slowly added to the clear solution, and the mixture was refluxed for 30 min. This solution was added dropwise over a period of 2 h to 2-chloroethanol (58.77 g, 730 mmol) and refluxing continued for 2 h. NaCl was removed by filtration, the solvent evaporated *in vacuo* and the residue purified over a silica gel column with diethylether/acetone 4:1 as eluent to yield 20.95 g (74%) of **12** as a colorless oil: IR (cm^{-1}, KBr pellet): 3358 (s), 2918 (s), 1418 (m). ^1H NMR (in $CDCl_3$, δ): 3.75 (t, 4H), 3.07 (s, 2H,), 2.70 (t, 4H), 2.65 (t, 4H), 1.87 (m, 2H). ^{13}C NMR (in $CDCl_3$, δ): 61.2, 35.2, 30.88, 29.69; Anal. Calcd for $C_7H_{16}O_2S_2$: C, 42.83; H, 8.21. Found: C, 42.53, H, 8.15. MS (*m*/*e*): 196 (theoretical for $C_7H_{16}S_2O_2$ 196.3).

Preparation of 3,7-Dithia-1,9-dichlorononane (13). (*Caution*! The product is a very harmful, blister-causing mustard compound). 3,7-

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Dithia-1,9-nonanediol (10 g, 51 mmol) was dissolved in 50 mL of dry CH_2Cl_2. Thionyl chloride (15.00 g, 126.1 mmol) was slowly added with a syringe and the yellow reaction mixture stirred at room-temperature for 1 h. Saturated $NaHCO_3$ was added very slowly until neutralization, and the organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo* to yield 10.94 g (92%) of an orange oil. The purity was about 90% (checked by GC) but for safety reasons no further purification was performed. IR (cm^{-1}, KBr pellet): 2954 (s), 2850 (s), 1440 (s), 1342 (m), 1298 (s), 1256 (s), 1128 (m), 1038 (m), 856 (m), 695 (s). ^1H NMR (in $CDCl_3$, δ): 3.62 (t, 4H), 2.83 (t, 4H), 2.65 (t, 4H), 1.84 (m, 2H). MS (*m*/*e*): 233 (theoretical for $C_7H_{14}S_2Cl_2$ 233.2).

Preparation of 3,6,9,12,15,18-Hexathiacyclononadecanol (1). Dried and finely powdered Cs_2CO_3 (14.14 g, 43.4 mmol) was suspended in 2500 mL of freshly distilled *N*,*N*-dimethylformamide (DMF). This solution was heated to 60 °C. **11** (5.30 g, 21.7 mmol) and **9** (4.76 g, 21.7 mmol) were separately dissolved in 500 mL of freshly distilled DMF and transferred under N_2 to two dropping funnels. Over a period of 80 h the two solutions were dropped simultaneously into the reaction vessel. After end of addition, the mixture was allowed to stir for another 24 h at room temperature. DMF was removed with a Rotovapor and the residue extracted with 200 mL of CH_2Cl_2 and filtered to remove polymers and cesium salts. CH_2Cl_2 was removed *in vacuo* and the remaining brown wax extracted with 5 × 150 mL of hot ethanol. The combined fractions were stored at −20 °C over several days during which period a yellow white solid formed. This material was repeatedly recrystallized with ethanol to yield **1** as a microcrystalline solid (2.71 g, 32%). IR (cm^{-1}, KBr pellet): 3444 (s), 2924 (s), 1418 (s), 1262 (s), 1194 (m), 1134 (w), 1036 (s), 992 (m), 816 (w), 702 (m), 680 (m). ^1H NMR (in $CDCl_3$, δ): 3.84 (q, 1H), 2.5−3 (m, 25H). ^{13}C NMR (in $CDCl_3$, δ): 70.62, 37.79, 32.67, 32.12, 32.09, 32.08, 32.02. Anal. Calcd for $C_{13}H_{26}OS_6$: C, 39.97; H, 6.71 S, 49.24. Found: C, 39.89; H, 7.05; S, 49.00. MS (*m*/*e*): 390 (theoretical for $C_{13}H_{26}S_6O$ 390.7).

Preparation of 3,6,9,13,16,19-Hexathiacycloicosanol (2). The procedure is identical to that described for **1**. The educt compounds were **9** (5.50 g, 22.5 mmol) and **13** (5.25 g, 22.5 mmol). Compound **2** was isolated as a white crystalline solid (3.18 g, 35%). IR (cm^{-1}, KBr pellet): 3412 (m), 2950 (s), 1418 (s), 1250 (w), 1192 (s), 1136 (m), 1064 (w), 1034 (s), 988 (w), 836 (w), 812 (w), 724 (w), 694 (m). ^1H NMR (in $CDCl_3$, δ): 3.88 (q, 1H), 2.5−3.5 (m, 24H), 3,01 (s, 1H), 1.88 (q, 2H). ^{13}C NMR (in CD_3CN, δ): 70.55, 37.67, 32.63, 31.94, 31.79, 31.73, 30.16, 29.88. Anal. Calcd for $C_{14}H_{28}OS_6$: C, 41.54; H, 6.97; S, 47.53. Found: C, 41.67; H, 6.84; S, 47.93; MS (*m*/*e*): 404 (theoretical for $C_{14}H_{28}S_6O$ 404.7).

Preparation of [Ag(19-aneS6-OH)][CF_3SO_3] (3). **1** (50 mg, 0.13 mmol) was dissolved in 10 mL of hot ethanol. To this solution was added [Ag][O_3SCF_3] (33 mg, 0.13 mmol) dissolved in 2 mL of water dropwise. After 10 min of refluxing, the solution was allowed to cool and solvents removed *in vacuo*. The remaining white solid was stirred with CH_2Cl_2 to remove any unreacted **1** and filtered to yield **3** as a white powder (72 mg, 88%). IR (cm^{-1}, KBr pellet): 3446 (s), 2908 (m), 1628 (m), 1424 (m), 1252 (s), 1174 (s), 1074 (m), 1036 (s), 648 (s), 580 (m), 520 (m). ^1H NMR (in CD_3CN, δ): 4.36 (q, 1H), 3−3.3 (m, 26H). ^{13}C NMR (in CD_3CN, 293 K, δ)SPCLN 67.82, 36.58, 31.62, 31.48, 30.84, 30.77, 30.73. (in CD_3CN, 218 K, δ): 66.38, 34.84, 30.53, 30.16, 29.64, 29.57, 29.52. Anal. Calcd C, 25.96; H, 4.05; S,34.66. Found: C, 26.25; H, 4.18; S, 34.69; MS (*m*/*e*): 498 (theoretical for $C_{13}H_{26}S_6OAg$ 498.6).

Preparation of [Ag(20-aneS6-OH)][BF_4] (4). **2** (50 mg, 0.12 mmol) was dissolved in 5 mL of THF, and $AgBF_4$ (23 mg, 0.12 mmol) in 2 mL of THF was added dropwise. After 30 min of stirring at room temperature, the solvent was removed *in vacuo* to yield **4** as a white powder (65 mg , 90%). IR (cm^{-1}, KBr pellets): 3428 (m), 2918 (m), 1418 (m), 1218 (w), 1194 (w), 1034 (s), 692 (w), 526 (w). ^1H NMR (in CD_3CN, δ): 4.07 (q, 1H), 2.7−3.2 (m, 25H), 2.1 (q, 2H). ^{13}C NMR (in CD_3CN, 293 K, δ): 68.29, 36.70, 31.68, 31.63, 31.46, 31.27, 29.92, 26.01. ^{13}C NMR (in CD_3CN, 218 K, δ): 67.84, 35.44, 31.22, 30.97, 30.85, 30.40, 28.46, 25.12. Anal. Calcd for $C_{14}BF_4H_{28}S_6OAg$: C, 28.05; H, 4.71; S, 32.10. Found: C, 28.12; H, 4.59; S, 32.29. MS (*m*/*e*) 512 (theoretical for $C_{14}H_{28}S_6OAg$ 512.6).

Table 1. Crystallographic Data for **3** and **4**

	3	**4**
formula	$AgC_{14}F_3H_{26}O_4S_7$	$AgBC_{14}F_4H_{28}OS_{16}$
fw	647.64	599.40
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	10.760(1)	10.076(4)
b, Å	10.853(2)	10.525(3)
c, Å	11.326(2)	22.135(8)
α, deg	78.73(1)	93.32(2)
β, deg	73.47(1)	102.43(2)
γ, deg	74.99(1)	100.32(2))
V, Å^3	1214.0(4)	2243.9(14)
Z	2	4
T, °C	20	−70
ρ_{calcd}, g cm^{-3}	1.772	1.774
μ, mm^{-1}	1.2757	1.493
F(000)	656	1216
R^a	0.0494	0.0654
$R_w{}^b$	0.0501[26]	0.1672

[a] $R_w = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $w^{-1} = 1/[\sigma^2(F_o{}^2) + (0.102P)^2 + 11.97P$, $P = (F_o{}^2 + 2\ F_c{}^2)/3$.[26]

Table 2. Some Selected Bond Lengths (Å) and Angles (deg) for the Complex Cation **3** with Esd's in Parentheses

Ag(1)−S(2)	2.644(2)	S(2)−C(4)	1.81(1)
Ag(1)−S(3)	2.573(2)	S(3)−C(5)	1.793(9)
Ag(1)−S(5)	2.655(3)	S(3)−C(6)	1.813(9)
Ag(1)−S(6)	2.551(2)	S(4)−C(7)	1.79(1)
Ag(1)−S(1)	3.553	S(4)−C(8)	1.79(1)
Ag(1)−S(4)	3.269	S(5)−C(9)	1.821(9)
S(1)−C(1)	1.810(9)	S(5)−C(10)	1.805(9)
S(1)−C(13)	1.800(9)	S(6)−C(11)	1.79(1)
S(2)−C(4)	1.81(1)	S(6)−C(12)	1.805(8)
S(3)−Ag(1)−S(2)	83.88(7)	C(4)−S(2)−Ag(1)	97.7(3)
S(5)−Ag(1)−S(2)	104.05(8)	C(5)−S(3)−Ag(1)	102.7(3)
S(5)−Ag(1)−S(3)	133.05(8)	C(6)−S(3)−Ag(1)	104.9(3)
S(6)−Ag(1)−S(2)	139.02(7)	C(9)−S(5)−Ag(1)	110.2(3)
S(6)−Ag(1)−S(3)	118.52(8)	C(10)−S(5)−Ag(1)	97.5(3)
S(6)−Ag(1)−S(5)	85.57(8)	C(11)−S(6)−Ag(1)	99.5(3)
C(3)−S(2)−Ag(1)	109.1(3)	C(12)−S(6)−Ag(1)	111.8(3)

Structure Determination of [Ag(19-aneS6-OH)][CF_3SO_3] (3). A colorless crystal (0.1 × 0.12 × 0.2 mm) of [Ag(19-aneS6-OH)][CF_3SO_3] was obtained by slow diffusion of diethylether into methanol. The crystal used for X-ray measurements was sealed in a glass capillary. X-ray data were collected on a CAD 4 diffractometer (ENRAF Nonius) using graphite-monochromated CuKα radiation ($\lambda = 1.54178$ Å). Unit cell parameters were determined by the least squares method using 22 carefully centered independent reflections. Intensity data were collected by the $\omega/2\theta$ method in the range of $4.98° < 2\theta < 77.49°$. The intensity of 5322 reflections were measured, of which 5057 had $I > 3\sigma(I)$. The usual corrections were applied. The absorption correction was determined by ψ-scans. The structure was solved by the Patterson technique using the program set CRYSTALS.[25] All subsequent calculations were carried out on a VAXstation 3100 using the same set of programs. Anisotropic least-squares refinement was carried out on all non-hydrogen atoms. The hydrogen atoms are in calculated positions with a fixed distance of 1.0 Å. A Chebychev weighting scheme has been applied.[26] Scattering factors were taken from ref 27. The hydroxylic oxygen atom is found in both possible positions with a ratio of about 2:1. For both positions the occupancy was refined holding the sum equal to 1. A summary of the crystal data is given in Table 1. Selected bond distances and angles are listed in Table 2, with atomic coordinates in Table 3. The ORTEP presentation of the complex cation generated by the program SNOOPI[28] is given in Figure 1. The oxygen is depicted in the position of higher occupancy.

Structure Determination of [Ag(20-aneS6-OH)][BF_4] (4). A colorless crystal (0.3 × 0.3 × 0.1 mm) of [Ag(20-aneS6-OH)][BF_4]

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Table 3. Final Fractional Coordinates and Equivalent Isotropic Thermal Parameters for Compound **3** (Esd's in Parentheses)

atom	x/a	y/b	z/c	U_{eq},[a,b] Å^2
Ag(1)	0.22586(9)	0.4623(3)	0.2240(8)	0.0689(3)
S(1)	0.1117(2)	0.7889(2)	0.2774(2)	0.0663(1)
S(2)	0.3782(2)	0.4779(2)	0.3648(2)	0.0637(1)
S(3)	0.0968(2)	0.3504(2)	0.4262(2)	0.0597(1)
S(4)	0.1173(3)	0.2324(2)	0.1647(3)	0.0747(1)
S(5)	0.3962(9)	0.3757(2)	0.0222(2)	0.0644(1)
S(6)	0.0959(2)	0.6092(2)	0.0745(2)	0.0588(1)
C(1)	0.2903(9)	0.7701(8)	0.2378(8)	0.0587(3)
C(2)	0.3419(8)	0.7414(9)	0.3542(9)	0.0647(3)
C(3)	0.308(1)	0.6218(9)	0.4398(9)	0.0679(3)
C(4)	0.329(1)	0.3553(9)	0.491(1)	0.0701(3)
C(5)	0.180(1)	0.3621(9)	0.5384(8)	0.0675(3)
C(6)	0.147(1)	0.1805(8)	0.4099(9)	0.0689(3)
C(7)	0.083(1)	0.1506(9)	0.320(1)	0.0844(4)
C(8)	0.288(1)	0.1561(9)	0.108(1)	0.0742(3)
C(9)	0.359(1)	0.2318(9)	−0.0065(9)	0.0759(4)
C(10)	0.3307(9)	0.4969(9)	−0.0910(9)	0.0680(3)
C(11)	0.1796(9)	0.5360(9)	−0.0639(9)	0.0670(3)
C(12)	0.1412(9)	0.7638(8)	0.0293(9)	0.0631(3)
C(13)	0.0765(9)	0.8503(8)	0.1281(9)	0.0624(3)
O(1)	0.4777(8)	0.7244(9)	0.3238(8)	0.0725(3)
O(1a)	0.298(2)	0.845(2)	0.417(2)	0.0777(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Variances are calculated according to ref 45.

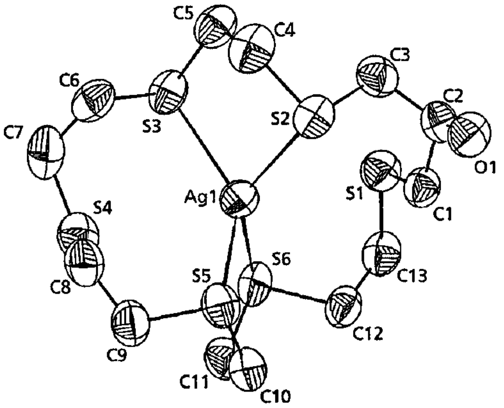

Figure 1. Thermal motion ellipsoids (50% probability) of the complex cation **3**. The oxygen O(1) is depicted in the position of higher probability.

was obtained by slow diffusion of diethylether into methanol. X-ray data were collected on a CAD 4 diffractometer (ENRAF Nonius) using graphite-monochromated MoKα radiation ($\lambda = 0.7107$ Å). Intensity data were collected at 203 K with ω-scans in the range $6.06° < 2\theta < 54.20°$. The intensity of 10 558 reflections were measured, of which 7783 had $I > 2\sigma(I)$. The unit cell parameters were obtained through a least-squares analysis of 25 reflections in the θ range 8.05−12.53°. Reflections were corrected for Lorentz polarization and for absorption by DIFABS[29] ($T_{min} = 0.9819$ and $T_{max} = 9.9997$). Three standard reflections were monitored for decay every 300 reflections; a decrease in intensity of 4.8% was detected and considered in the further structure calculations. Crystal data are given in Table 1.

The structure was solved by the heavy-atom Patterson techniques (SHELXS 86[30]). The refinement was performed using SHELXL 93[31] applying the final weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.102P)^2 + 11.97P]$ where $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were calculated with anisotropic temperature factors. Hydrogen atoms were calculated for idealized positions and refined using the "*riding model*" option in SHELXL 93. Two independent molecules (**4a** and **4b)** of [Ag(20-aneS6-OH)](BF$_4$) are contained in the asymmetric unit. The position of the hydroxyl group in the macrocyclic ring system is disordered between the carbon atoms C(3) and C(13) (and C(43) and C(33), respectively). Pictures demonstrating this disorder are included in the Supporting Information. The occupancy of these positions has been refined by means of a free variable which gives evidence for a disorder ratio of approximatly 0.6/0.4. An ORTEP representation of the two crystallographically independent complex cations **4a** and **4b** together with the molecular labeling scheme is given in Figure 2, with important bond lengths in Table 4 and atomic coordinates in Table 5.

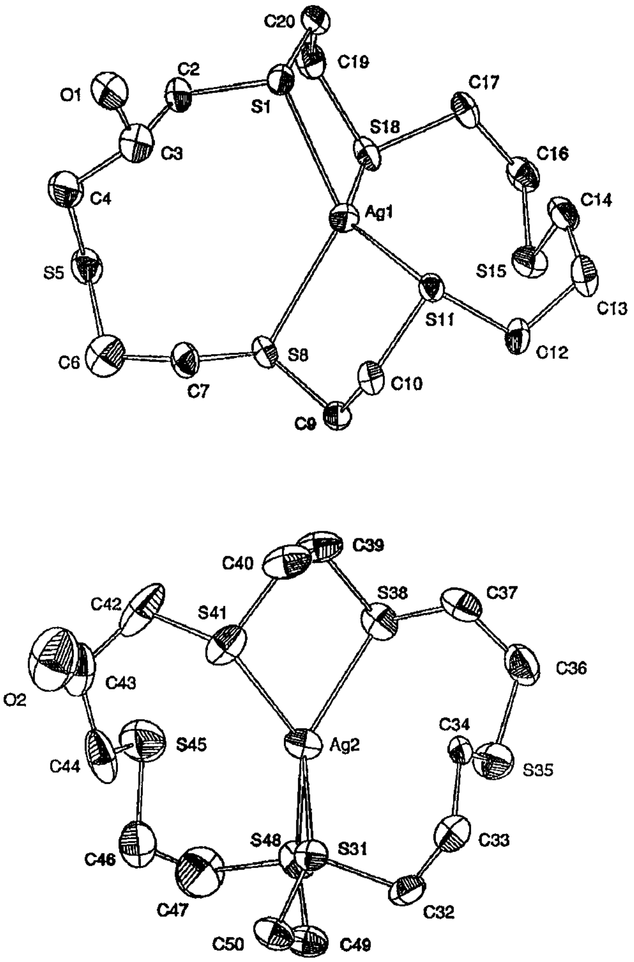

Figure 2. Thermal motion ellipsoids (50% probability) of the two crystallographically independent complex cations **4a** (top) and **4b** (bottom). The oxygen atoms O(1) and O(2) are depicted in the position of higher probability.

Results

Synthesis of 1 and 2 and Complex Formation. Due to the increasing interest in macrocyclic thio crowns, a wide variety of synthetic approaches have been developed and described. For systems with three sulfur atoms the template approach using the "*fac*-Mo(CO)$_3$" fragment is most favorable, and only recently was this approach extended to derivatized [9-aneS3-R] systems[32−34] bearing hydroxyl groups at the C backbone. For macrocycles with four sulfur atoms, different ring sizes have been described and at least one study has also been performed with water soluble hydroxyl derivatized systems.[35] For the latter

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for the Complexes **4a** and **4b** with Esd's in Parentheses

4a		**4b**	
Ag(1)−S(1)	2.578(2)	Ag(2)−S(31)	2.685(2)
Ag(1)−S(11)	2.586(2)	Ag(2)−S(41)	2.725(2)
Ag(1)−S(8)	2.597(2)	Ag(2)−S(38)	2.582(2)
Ag(1)−S(18)	2.598(2)	Ag(2)−S(48)	2.604(2)
Ag(1)−S(5)	3.427(2)	Ag(2)−S(45)	4.502(2)
Ag(1)−S(15)	3.568(3)	Ag(2)−S(35)	3.719(2)
S(1)−C(20)	1.799(6)	S(31)−C(50)	1.801(7)
S(1)−C(2)	1.810(6)	S(31)−C(32)	1.826(7)
C(4)−S(5)	1.819(10)	C(34)−S(35)	1.900(7)
S(5)−C(6)	1.807(9)	S(35)−C(36)	1.778(8)
C(7)−S(8)	1.829(6)	C(37)−S(38)	1.820(8)
S(8)−C(9)	1.814(6)	S(38)−C(39)	1.802(8)
S(11)−C(12)	1.824(6)	C(40)−S(41)	1.790(8)
C(10)−S(11)	1.807(6)	S(41)−C(42)	1.823(8)
C(14)−S(15)	1.821(7)	C(44)−S(45)	1.668(8)
S(15)−C(16)	1.803(6)	S(45)−C(46)	1.826(10)
C(17)−S(18)	1.818(6)	C(47)−S(48)	1.828(10)
S(18)−C(19)	1.814(6)	S(48)−C(49)	1.793(7)
S(1)−Ag(1)−S(11)	119.48(5)	S(38)−Ag(2)−S(48)	121.59(6)
S(1)−Ag(1)−S(8)	122.13(5)	S(38)−Ag(2)−S(31)	136.14(6)
S(11)−Ag(1)−S(8)	86.78(5)	S(48)−Ag(2)−S(31)	82.70(6)
S(1)−Ag(1)−S(18)	84.71(5)	S(38)−Ag(2)−S(41)	82.52(7)
S(11)−Ag(1)−S(18)	135.22(5)	S(48)−Ag(2)−S(41)	147.44(7)
S(8)−Ag(1)−S(18)	112.88(5)	S(31)−Ag(2)−S(41)	94.24(6)

Table 5. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Compound **4a** and **4b** (Esd's in Parentheses)

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
		Compound **4a**		
Ag(1)	0.2611(1)	0.1966(1)	0.0182(1)	0.031(1)
S(1)	0.1120(1)	0.3710(1)	-0.0039(1)	0.024(1)
S(5)	0.2894(2)	0.2881(2)	−0.1753(1)	0.035(1)
S(8)	0.3339(1)	0.0707(1)	−0.0697(1)	0.024(1)
S(11)	0.1510(1)	−0.0273(1)	0.0460(1)	0.023(1)
S(15)	0.4990(2)	0.1446(2)	0.1644(1)	0.035(1)
S(18)	0.4541(1)	0.3892(2)	0.0762(1)	0.027(1)
C(2)	0.1458(7)	0.4257(6)	-0.0762(3)	0.029(1)
C(3)	0.0576(11)	0.3283(8)	−0.1303(4)	0.058(2
C(4)	0.1194(11)	0.3314(8)	−0.1871(4)	0.060(2)
C(6)	0.2485(10)	0.1138(8)	−0.1931(4)	0.057(2)
C(7)	0.2038(6)	0.0349(6)	−0.1433(3)	0.030(1)
C(9)	0.3061(6)	−0.0866(5)	−0.0402(3)	0.025(1)
C(10)	0.1687(6)	−0.1230(5)	−0.0212(3)	0.025(1)
C(12)	0.2657(7)	−0.0933(6)	0.1063(3)	0.030(1)
C(13)	0.2703(8)	−0.0339(7)	0.1714(3)	0.038(2)
C(14)	0.3287(7)	0.1092(6)	0.1822(3)	0.034(1)
C(16)	0.5484(6)	0.3150(6)	0.1915(3)	0.032(1)
C(17)	0.4543(7)	0.3991(6)	0.1585(3)	0.031(1)
C(19)	0.3716(6)	0.5244(6)	0.0537(3)	0.030(1)
C(20)	0.2170(6)	0.5024(6)	0.0510(3)	0.028(1)
O(1)	−0.0773(8)	0.3524(8)	−0.1498(4)	0.038(2)
O(2)	0.3745(18)	0.7041(16)	0.2256(6)	0.100(5)
		Compound **4b**		
Ag(2)	0.6612(1)	0.4997(1)	0.4026(1)	0.045(1)
S(31)	0.8173(2)	0.4510(2)	0.3231(1)	0.031(1)
S(35)	0.7475(2)	0.2087(2)	0.4398(1)	0.049(1)
S(38)	0.4901(2)	0.3630(2)	0.4565(1)	0.038(1)
S(41)	0.4275(2)	0.4856(2)	0.3116(1)	0.045(1)
S(45)	0.6242(3)	0.7848(3)	0.4027(2)	0.076(1)
S(48)	0.8948(2)	0.6402(2)	0.4659(1)	0.039(1)
C(32)	0.9069(7)	0.3174(7)	0.3425(3)	0.038(1)
C(33)	0.8071(8)	0.1867(7)	0.3242(4)	0.044(2)
C(34)	0.6790(6)	0.1640(6)	0.3528(3)	0.029(1)
C(36)	0.5988(9)	0.1405(8)	0.4666(4)	0.051(2)
C(37)	0.4684(8)	0.1883(7)	0.4393(4)	0.045(2)
C(39)	0.3261(7)	0.3853(9)	0.4111(3)	0.048(2)
C(40)	0.3104(7)	0.3705(9)	0.3413(3)	0.048(2)
C(42)	0.3548(10)	0.6298(11)	0.3217(4)	0.068(3)
C(43)	0.4321(11)	0.7447(8)	0.2955(4)	0.058(2)
C(44)	0.6034(11)	0.7806(8)	0.3258(4)	0.060(2)
C(46)	0.8074(10)	0.8531(8)	0.4101(4)	0.057(2)
C(47)	0.8937(12)	0.8125(9)	0.4598(6)	0.035(2)
C(47)	0.8937(12)	0.8125(9)	0.4598(6)	0.086(4)
C(49)	1.0152(7)	0.6105(7)	0.4202(3)	0.040(2)
C(50)	0.9593(7)	0.5867(7)	0.3501(3)	0.040(2)
O(11)	0.1418(14)	−0.0552(14)	0.1856(6)	0.060(5)
O(21)	0.8684(32)	0.0876(27)	0.3388(22)	0.197(19)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

systems the [1 + 1] cyclization was applied using $[K]^+$ as a potential template. For macrocycles with $S \geq 4$ the [2 + 2] and the [1 + 1] approach are described, the latter being templated usually by $[Cs]^+$. The yield-determining ring closure step results usually in higher yields with the [1 + 1] cyclization but the fragments have to be prepared separately. We have chosen this approach as we wanted to introduce a derivatized functional group at only one C-backbone and the [2 + 2] approach would lead to compounds with two functional groups and different stereoisomers. Our synthetic approach (Scheme 1) to derivatized 19- and 20-membered rings is based on the derivatized "$[S_4]$" fragment **9** which, in combination with the "$[S_2X_2]$" moieties **11** and **13** allow the synthesis of ligands **1** and **2**.

Although yields are moderate they are nevertheless relatively high in comparison to those seen for other protocols. The fact that the yield decreased reproducibly with increasing ring size seems to be based on the weaker template effect provided by $[Cs]^+$ for larger ring sizes . This observation is in agreement with the general tendency previously described elsewhere.[36] In addition to the influence of the cation on the ring closure step the purity of the $[S_2X_2]$ moieties **11** and **13** are most important. These extremly toxic substances tend to decompose in the presence of impurities during the long reaction period, thus decreasing yield significantly, whereas the $[S_4]$ fragment **9** is relatively stable. In contrast to tetradentate hydroxyl derivatized thio crowns,[35] [19-aneS6-OH] is not soluble in water and complexation studies could only be performed in polar organic solvents. In methanol or acetonitrile complexation is completed within a few minutes at room temperature, as is evident by the rapid stabilization of the measured potential. This behavior reflects, on the one hand, the known lability of coordinated solvent molecules and, on the other hand, the known *endo* conformation of two sulfur atoms in the free ligands,[37] which favors quick encapsulation of metal ions. The S6 ligands are thus preformed for encapsulating $[Ag]^+$ and no strong steric rearrangements have to be performed to bring the $[Ag]^+$ center in the cavity of the ligand although the other four sulfur atoms are *exo* orientated. This prearrangement seems also to be responsible for the fact that almost no polymers are formed. Recomplexation to monomers would demand enhanced activation energy and be consequently slow.

X-Ray structure of [Ag(19-aneS6-OH)][CF$_3$SO$_3$]. Colorless crystals of **3**, suitable for X-ray structure analysis could be grown from methanol/diethylether by the slow diffusion method. The complex crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, thus one complex cation is in the asymmetric unit of the cell. An ORTEP presentation of the complex cation is given in Figure 1. The structure exhibits the $[Ag]^+$ center in a strongly distorted tetrahedral coordination geometry with bonds to four of the six sulfur atoms forming two five-membered chelates and a nine- and an eight-membered ring respectively. Analysis of the bond lengths reveals that two Ag−S bonds are short (Ag−S(3) = 2.573(2)Å and Ag−S(6) = 2.551(2) Å) and two bonds

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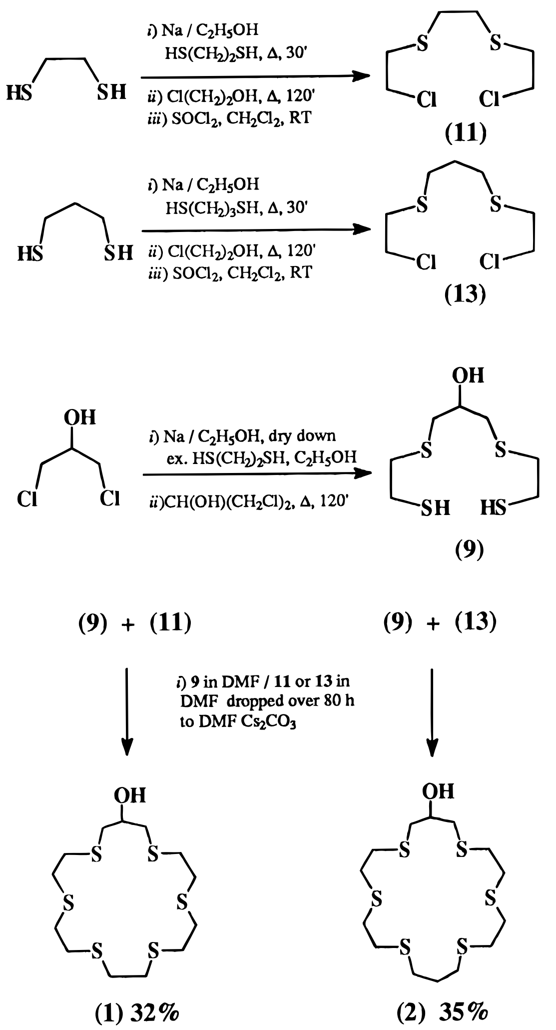
(36) Buter, J.; Kellog, R. M. J. *J. Org. Chem.* **1981**, *46*, 4481

(37) Hartman, J. R.; Wolf, R. E.; Foxman, B.; Cooper, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 131.

Scheme 1



are long (Ag−S(2) = 2.644(2) Å and Ag−S(5) = 2.655(3) Å), and in addition all bond lengths are significantly different from each other. A similar observation can be made with the angle distribution. Very strong deviations from the ideal *tetrahedral* angle are observed: two very compressed angles of 83.88(7) (S(3)−Ag−S(2)) and 85.57(8)°(S(6)−Ag−S(5)) and two large angles of 133.05(8) (S(5)−Ag−S(3)) and 139.02(7)° (S(6)−Ag−S(2)). The distances to the remaining two sulfur atoms are 3.553 (Ag−S(1)) and 3.265 Å (Ag−S(4)), which are much longer than the sum of the covalent *radii* of the two atoms (2.99 Å), and consequently no interaction is expected.

X-Ray Structures of [Ag(20-aneS6-OH)][BF$_4$]. Colorless crystals of **4** suitable for *X*-ray structure analysis could be grown from methanol/diethylether by the slow diffusion method. The complex crystallizes in the triclinic space group $P\bar{1}$ with $Z = 4$; thus, two complex cations are contained in the asymmetric unit of the cell. An ORTEP presentation of the two complex cations **4a** and **4b** is given in Figure 2. Structural features in the two cations are comparable to those found in complex **3**. Both [Ag]$^+$ centers are found in a strongly distorted tetrahedral geometry with four sulfur atoms bound to the metal center. Again two five-membered chelates and two large nine-membered rings are formed. The bond lengths in **4** are not as asymmetric as in **3**. Two Ag−S bonds are short at 2.578(2) and 2.586(2) Å (Ag(1)−S(1) and Ag(1)−S(11) respectively) and two are long at 2.597(2) and 2.598 Å (Ag(1)−S(8) and Ag(1)−S(18), respectively). As expected one short Ag−S distance and one long Ag−S distance are found within each of the two five-membered chelate rings. The two angles of the five-membered chelate rings again are strongly compressed at 86.78(5) and 84.71(4)°, respectively. The second cation shows a different behavior in that the Ag−S bond length distribution is strongly asymmetric and ranges from one short distance of 2.582(2) Å (Ag(2)−S(38) over two medium distances of 2.604(2) and 2.685(2) Å for Ag(2)−S(48) and Ag(2)−S(31) respectively to one long at 2.725(2) Å for Ag(2)−S(41). One of the five-membered chelate rings comprises the shortest and the longest distance, whereas the other ring contains the two medium bond lengths. The average bond length found in each ring are thus quite similar at 2.653(2) and 2.648(2) Å. As a consequence of this asymmetry, the differences between the compressed and stretched angles are larger than in **3**. The two angles at the silver center of the five-membered chelates are with 82.70(6) and 82.52(7)° significantly smaller and the angles of the nine-membered rings with 136.14(6) and 147.44(6)° but much larger than in **3** or in **4a**. In both complex cations the distances to two sulfur atoms range between 3.088 Å (Ag(2)−S(41)) and 4.503 Å (Ag(1)−S(5)), thus is larger than the sum of the covalent radii and can not be considered as real Ag−S bonds.

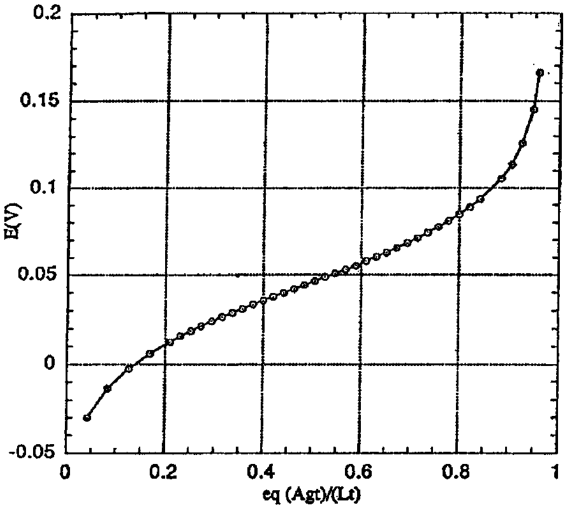


Figure 3. Typical titration curve (E *vs* [Ag]$_{tot}$/[L]$_{tot}$) for the determination of K_1

Scheme 2

$$[\mathrm{Ag}]^+ \;+\; [\mathrm{L}] \;\rightleftharpoons\; [\mathrm{AgL}]^+$$

$$K_1 = \frac{[\mathrm{AgL}]^+}{[\mathrm{Ag}]^+ \times [\mathrm{L}]}$$

Stability Constants. The stability constants K_1 for the complexation reaction with L = **1**, **2**, and **5** described in Scheme 2 were determined by pAg potentiometric titrations.

For all three ligands it was found that the *equilibrium* was established within a few minutes as demonstrated by the readily achieved stability of the potential, which remained constant even over extended time periods. A sharp jump was observed after the addition of 1 equiv of [Ag]$^+$ per ligand indicating 1:1 stochiometry of the process. A typical titration curve is depicted in Figure 3. The stability constants together with some representative and comparable literature values are given in Table 6. It was found that **5** forms the most stable complex of 1:1 stochiometry with log K_1 12.67 ± 0.13. For **1** log K_1 was found to be 12.04 ± 0.19 and for **2** 11.49 ± 0.15.

Table 6. Selected Stability Constants of Macrocycles with $[Ag]^+$ Determined in Methanol and in Water

[L]	log K_1	ref
[15-aneS4][a]	7.41 ± 0.04	20
[16-aneS4][a]	7.56 ± 0.08	20
[18-aneS6][a]	12.67 ± 0.13	this work
[12-aneN2S2][b]	10.95	21
[14-aneN2S2][b]	8.08	21
[16-aneN2S2][b]	7.28	21
[18-aneN2S2][b]	13.7	22
[18-aneN4S2][b]	14.1	22
[19-aneS6-OH][a]	12.04 ± 0.19	this work
[20-aneS6-OH][a]	11.49 ± 0.15	this work

[a] In methanol. [b] In water.

Discussion

One of the most interesting features in the complexes **3** and **4** is the fact that the solid state structure reveals only *tetrahedral* coordination geometry and not, as expected from the X-ray structure of $[Ag(18\text{-ane-S6})]^+$, an octahedral geometry.[13] Since the synthetic conditions, in particular solvent and temperature, were similar, one can suppose that the different geometry is a thermodynamic characteristic and not the result of different intermediate solvents coordination, influencing the mode of encapsulating the metal center. Modeling studies of the noncoordinated sulfur atoms reveal that one of the two lone pairs is directed toward the $[Ag]^+$ center, but coordination nevertheless is not achieved. Simple electron counting would lead to the assumption that a metal center with d^{10} electron configuration such as $[Ag]^+$ will accept four 2-electron-donating ligands to fulfill the 18-e^- rule. This assumption is obviously not true since a number of octahedral $[Ag]^+$ complexes are known. Although the electronic properties of the sulfur atom in thioether moieties depend strongly upon the interacting metal, three possible binding modes must be considered. On the basis of sp^3 hybridization at the "R_2S" moiety, the sulfur is able to act as a two-electron σ-donating ligand. If metal orbitals of appropriate energy and symmetry are empty the two lone pairs can act additionally as a π-donating ligand. Furthermore it can also provide appreciable π-accepting properties into orbitals of π^* symmetry (with respect to the M−S bond) rather then into empty d-orbitals which are too high in energy,[38,39] thus weakening the M−S bond energy. As a consequence of this qualitative consideration, it must be concluded that Ag(I) complexes with a coordination number higher than 4 exhibit significantly longer bond distances than comparable complexes of coordination number = 4. This result is supported by the comparison of the structural data of **3** and **4** with the two prominent examples $[Ag(16\text{-aneS6})]^+$ (**8**)[12] and $[Ag(18\text{-aneS6})]^+$ (**6**). **8** exhibits a bond length distribution similar to that found in **3** or **4**. Two bond distances are long (average 2.560(3) Å) and two are short (average 2.539(3) Å). On the other hand, in **6** the distorted octahedral geometry can be described as [2 + 4] coordination with two short (2.6665(12) Å) and four long Ag−S distances (2.7813(10) Å). Thus all bonds are significantly longer than in **3**, **4**, or **6** although only **8** is able to encapsulate the Ag(I) center efficiently and to profit most from the macrocyclic effect. Similar features are found by comparing **3** and **4** with the recently described structure of the complex [Ag(18-aneN2S4)][40] (**9**). The coordination geometry in this complex has been described as [5+1] with one very long Ag−N bond (2.817(15) Å). Comparing the "AgS_4" geometry in **9** with **3** or **4** we found a surprising similarity between the two skeletons with the exception that all bond lengths in **9** are considerably longer than in **3** or **4**. This observation mirrors the strong σ-donating but poor π-accepting properties of the amine ligand atoms, and the long Ag−S distances in **9** are thus rather a result of the electronic properties than of steric requirements.

A very similar behavior is also found in [9-aneS3] (**10**) complexes. Due to its preformed *endodentate* structure, this ligand usually forms very stable complexes with a wide variety of metal centers. The *X*-ray structures of $[Ag(9\text{-aneS3})_2]^+$ (**11**)[41] and $[Ag_3(9\text{-aneS3})_3]^+$ (**12**)[42] have been determined. It was found that the bond lengths in octahedral coordinated **11** are relatively long with 2.697(5) and 2.753(4) Å, whereas in the tetrahedral coordinated trimer **12** all bond lengths are considerably shorter (2.595(4), 2.613(4), and 2.480(2) Å) and comparable to those found in **3** or **4**. As expected the only exception is the bridging thioether group with 2.724(2) Å. Similar results have been obtained for $[Ag]^+$ complexes of 2,5,8-trithia-*o*-benzenophane (TT[9]OB).[43] Depending on the counterion, the complex cation $[Ag[TT[9]OB)]^+$ crystallizes either in an octahedral geometry with six long Ag−S bonds (2.709−2.788 Å for X = $[ClO_4]^-$) or in a tetrahedral geometry with four short Ag−S bonds (2.476−2.600 Å) for X = $[CF_3SO_3]^-$). From these comparisons it can be concluded that not just steric requirements are responsible for much the tighter Ag−S distances in "$[Ag(crown)]^+$" with tetrahedral coordination than with octahedral geometry.

Comparison of the thermodynamic stability constants for $[Ag]^+$ complexes with **1**, **2**, and **5** revealed only relatively small differences of about 0.6 in log K_1. Assuming that tetrahedral coordination would be present in methanol solution, the chelate effect, which basically influences the entropy term, will not be very different in an eight- and a nine-membered ring (in **3**) and two nine-membered rings (in **4**) thus resulting in the observed comparable stability constants of the two complexes. On the other hand, the chelate effect should be significantly stronger for octahedral coordinated **6** with only five-membered rings. In addition the macrocyclic effect,[44] which is present in **6**, is almost negligible in **3** and **4** under the assumption of a tetrahedral structure in solution. Thus one would expect a much higher stability for **6** than for **3** and **4**, which should exhibit stabilities similar to those of [16-aneS4]. However, the stability constants of **3** and **4** are not much smaller than those determined for **6** which is octahedral coordinated. These results can be explained by a fluxional behavior in solution as shown in Scheme 3; thus all six sulfur atoms participate in coordination and a macrocyclic effect for all compounds determines the free formation enthalpy.

This deduction is furthermore supported by NMR measurements. Such type of fluxionality has recently been described for the tetrahedral complex $[Ag(16\text{-aneS6})]^+$ and has been proven by ^1H NMR spectroscopy.[12] ^{13}C NMR spectra at 293 K of **5** and **6** exhibited one single resonance at 3.50 and 1.89 ppm, respectively, demonstrating in particular the high symmetry of **6** in solution. In the case of **3** or **4** ^{13}C and ^1H NMR measurements performed at different temperatures (from 293 down to 218 K) exhibited the same fluxional features. In

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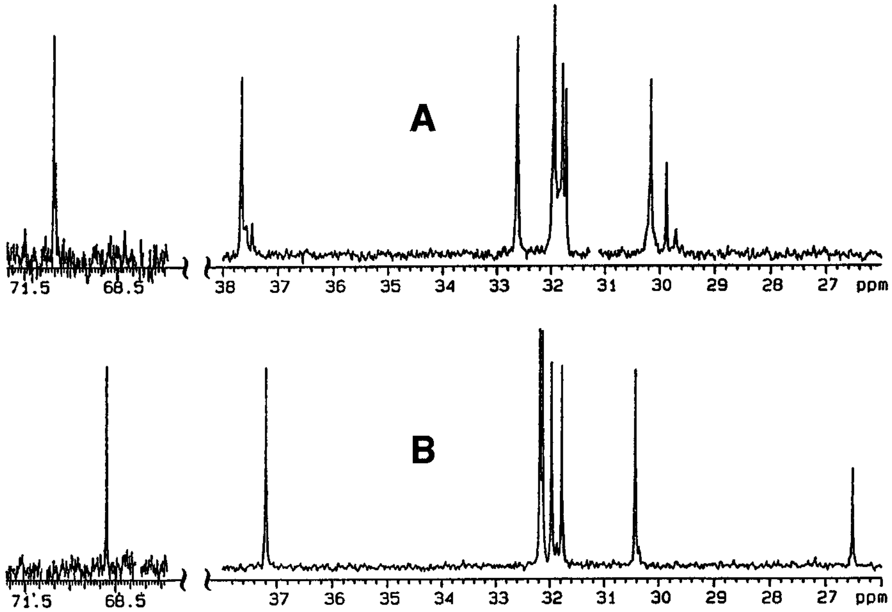
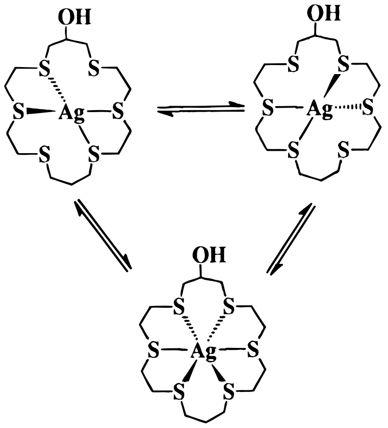


Figure 4. ^{13}C NMR spectra of the free ligand [20-aneS6-OH] (**A**) and of the complex [Ag(20-aneS6-OH]$^+$ (**B**) in CD_3CN at 293 K.

Scheme 3



particular ^{13}C NMR spectra of the free ligand **2** show as expected eight distinct resonances. A tetrahedral [Ag]$^+$ complex of **2** would have 14 lines, but only 8 lines could be detected down to temperatures of 218 K. The distribution pattern is similar to that found in **2**, but significantly shifted to lower field, thus clearly supporting the assumed fluxionality. Apart from a slight line broadening, no limiting spectra could be achieved neither for [Ag]$^+$ complexes of **1** or **2**. Two of these spectra are shown in Figure 4. The sharp quintett^{1}H-signal resulting from the $-CH_2-C\mathbf{H_2}-CH_2-$ group in **2** exhibited the same fully symmetrical form in the complex **4** over the observed temperature range but was shifted again by about 0.22 ppm to lower field.

It can be concluded from these measurements that **3**, **4**, and **6** have a fluxional octahedral coordination geometry in solution, although the former two crystallize in a tetrahedral geometry and the latter crystallizes in an octahedral geometry.

Conclusion

The two new Ag(I) complexes [Ag(19-aneS6-OH)]$^+$ and [Ag-(20-aneS6-OH]$^+$ were prepared and structurally characterized. Although they reveal *tetrahedral* coordination geometry in the solid state, we conclude from the determination of stability constants in methanol and ^{1}H- and ^{13}C NMR experiments, that fluxional behavior of the six sulfur atoms in solution results in an *octahedral* coordination geometry. The application of six-membered thio crowns for radioimmunotherapy with the isotope ^{111}Ag might therefore be promising, since *octahedral* coordination results in more efficient encapsulation of the Ag(I) ion than *tetrahedral,* as was obvious from molecular modeling studies. We are currently investigating the exchange rates of Ag(I) from these complexes in the presence of competing ligands which will allow definite conclusions about application of such complexes for nuclear medical purposes. The influence of the hydroxyl group or its derivatives in the β-position of the C-backbone on stability constants and coordination geometry is not yet elucidated and is currently under investigation.

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Supporting Information Available: Figures showing ^{13}C NMR spectra of the compounds **1**−**6** at different temperatures tables of crystal data, bond angles and distances, torsion angles, anisotropic parameters, and complete positional parameters, and figures showing ORTEP's exhibiting the observed disorder in **3** and in the two crystallographically independent cations **4a** and **4b**, as well as plots of the cell contents (31 pages). Ordering information is given on any current masthead page.

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