the energy of the metal d_π ("t_{2g}") orbitals, which are π^* with respect to metal–ligand bonding. Relative to complete N-ligation, this would increase the energy mismatch between these d orbitals and the bridging oxide p_π orbitals that mediate the π-superexchange mechanism, and hence decrease the magnitude of the antiferromagnetic exchange interaction. However, additional examples are required before such arguments can be entertained further.

An increase to 3 in the number of bridging oxides increases the magnitude of the antiferromagnetic exchange interaction to $-390\ \mathrm{cm^{-1}}$, whereas a decrease to a single oxide bridge decreases the magnitude of this interaction, in some cases becoming weakly ferromagnetic (positive J). Thus, the growing pool of mono-, bis-, and now tris(oxide)-bridged systems continues to support the belief that the number of oxide bridges (and its resulting influence on the Mn⋯Mn separation and Mn–O–Mn bridging angles) represents the single most important parameter influencing the magnitude of the magnetic exchange interactions in discrete oxide-bridged Mn complexes.

Electrochemistry. The electrochemical properties of complex **1** in DMF solution were investigated by the cyclic voltammetric technique. Two processes were observed, a reversible one-electron reduction at +0.66 V vs SCE ($i_c/i_a = 1.02$; $\Delta E_p = 110$ mV) and an irreversible reduction at $E_{p,c} = -0.47$ V. These observations define the three-component electron-transfer series of eq 3. These

$$\mathrm{Mn^{IV}Mn^{IV}} \xrightleftharpoons{+0.66\ \mathrm{V}} \mathrm{Mn^{III}Mn^{IV}} \xrightarrow{-0.47\ \mathrm{V}} \mathrm{Mn^{III}Mn^{III}} \tag{3}$$

values compare reasonably well with those found for $(NMe_4)[Mn_2O_2(pic)_4]$ in MeCN;[8] this compound is the one-electron-reduced version ($\mathrm{Mn^{III}Mn^{IV}}$) of complex **1**, and it displays a reversible one-electron oxidation to **1** at +0.53 V vs SCE and an irreversible reduction at −0.42 V.

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Registry No. **1**·MeCN, 122797-77-7; $[Mn_3O(OAc)_6(py)_3](ClO_4)$, 52705-71-2.

Supplementary Material Available: Complete listings of data collection and refinement parameters, crystal data, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and observed and calculated magnetic susceptibility data (6 pages); a list of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page. A complete MSC structure report (No. 87168) is available on request from the Indiana University Chemistry Library.

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Crown Thioether Chemistry. The Silver(I) Complexes of Trithia-9-crown-3, Trithia-12-crown-3, and Hexathia-18-crown-6

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The coordination chemistry of the three crown thioethers 1,4,7-trithiacyclononane (9S3), 1,5,9-trithiacyclododecane (12S3), and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) with Ag(I) has been investigated by structural and electrochemical methods. The bis complex $[Ag(9S3)_2](CF_3SO_3)$ contains a six-coordinate Ag(I) ion with Ag–S distances ranging from 2.696 (2) to 2.753 (1) Å. Chemical or electrochemical oxidation yields $[Ag(9S3)_2]^{2+}$, which has been studied by optical and EPR methods. The halide adducts [Ag(9S3)Cl] and [Ag(18S6)Br] both contain a tetrahedral AgS_3X core. In the former case, 9S3 coordinates in a tridentate fashion to yield a discrete, monomeric complex. In the latter, 18S6 provides two thioethers to one Ag(I) and a third to another to yield a polymeric chain. In $[Ag(12S3)](CF_3SO_3)\cdot MeCN$, each Ag(I) ion coordinates to three thioether groups (one from each of three independent 12S3 molecules) as well as a $CF_3SO_3^-$ counterion to yield distorted-tetrahedral geometry. In turn, the three ligand S atoms coordinate to different Ag(I) ions to generate a network structure. These results highlight the profound influence of ligand conformation on the structure and solution chemistry of their complexes. Crystal data: $[Ag(9S3)_2](CF_3SO_3)$, orthorhombic system, space group *Pnam*, $a = 7.884$ (2) Å, $b = 12.396$ (5) Å, $c = 23.546$ (7) Å, $Z = 4$; [Ag(9S3)Cl], monoclinic system, space group $I2/a$, $a = 14.144$ (2) Å, $b = 6.684$ (1) Å, $c = 22.277$ (2) Å, $\beta = 91.653$ (9)°, $Z = 8$; [Ag(18S6)Br], triclinic system, space group $P\bar{1}$, $a = 10.359$ (1) Å, $b = 10.420(1)$ Å, $c = 11.311(2)$ Å, $\alpha = 115.72$ (1)°, $\beta = 115.56$ (1)°, $\gamma = 82.62$ (1)°, $Z = 2$; $[Ag(12S3)](CF_3SO_3)\cdot MeCN$, orthorhombic system, space group $P2_12_12_1$, $a = 8.601(1)$ Å, $b = 14.224$ (3) Å, $c = 16.098$ (2) Å, $Z = 4$.

Introduction

Despite the strong affinity of thioether sulfur for silver,[1] little information is available concerning the crown thioether complexes of Ag(I).[2-4] We report here the reactions of Ag(I) with the tridentate crown thioethers 1,4,7-trithiacyclononane (9S3) and 1,5,9-trithiacyclododecane (12S3) and the hexadentate crown thioether 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) (Figure 1). These complexes attract interest since crown thioethers can induce unusual electronic and redox behavior (e.g., stabilization of low-spin Co(II), monomeric Rh(II), Pd(III), and Pt(III));[5,6] apparently the unique conformational properties of 9S3[7] impart high stability and novel structures to its complexes.

The stark contrast between the structural and electrochemical properties of the 9S3 complexes on one hand and those of 12S3 and 18S6 on the other underscores the critical role played by conformation in crown thioether chemistry.

Experimental Section

Physical Measurements. ^1H NMR spectra were recorded with a Bruker WH 300 spectrometer calibrated against residual solvent protons. Infrared spectra were recorded with a Perkin-Elmer 1710 FT spectrometer. EPR spectra were obtained with a Bruker ESP 300 spectrometer with the samples contained in quartz capillaries. UV–visible spectra were obtained with a Perkin-Elmer 552 spectrophotometer, with the sample temperature controlled through use of a jacketed cell. Elemental analyses

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Table I. Crystallographic Data for $[Ag(9S3)_2](CF_3SO_3)$, $[Ag(9S3)Cl]$, $[Ag(18S6)Br]$, and $[Ag(12S3)](CF_3SO_3)\cdot MeCN$

	$[Ag(9S3)_2](CF_3SO_3)$	$[Ag(9S3)Cl]$	$[Ag(18S6)Br]$	$[Ag(12S3)](CF_3SO_3)\cdot MeCN$
mol wt	617.61	323.7	548.53	472.41
space group	*Pnam*	*I*2/*a*	$P\bar{1}$	$P2_12_12_1$
a, Å	7.884 (2)	14.144 (2)	10.359 (1)	8.601 (1)
b, Å	12.396 (5)	6.684 (1)	10.420 (1)	14.224 (3)
c, Å	23.546 (7)	22.277 (2)	11.311 (2)	16.098 (2)
α, deg	90	90	115.72 (1)	90
β, deg	90	91.653 (9)	115.56 (1)	90
γ, deg	90	90	82.62 (1)	90
vol, Å^3	2301.0	2105.2	991.9	1969.4
d_{calc}, g/cm^3	1.78	2.04	1.84	1.59
Z	4	8	2	4
λ	Mo Kα	Cu Kα	Mo Kα	Mo Kα
μ, cm^{-1}	15.1	231.0	36.0	14.4
final *R*, %	3.96	5.99	2.56	3.01
final R_w, %	3.75	6.73	2.88	3.36
temp	ambient	ambient	ambient	ambient
max abs cor	1.08	1.52		1.62

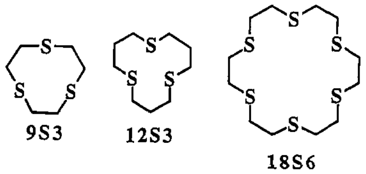

Figure 1. Ligands used in this work.

were performed by M. Gascoyne, J. Kench, and A. Douglas of the microanalytical service at the Inorganic Chemistry Laboratory, Oxford, England. Conductivity measurements were made on nitromethane or acetonitrile solutions with a PTI 18 digital conductivity meter calibrated against 0.01 M KCl.

Electrochemical measurements were performed with a Princeton Applied Research Model 175 programmer, Model 173 potentiostat, Model 179 digital coulometer, and Model RE 0074 X-Y recorder. Cyclic voltammetry was carried out with a glassy-carbon-disk or platinum-disk working electrode, a platinum auxiliary electrode, and a saturated calomel (SCE) reference electrode. Potentials were calibrated against ferrocene/ferrocenium as an internal standard (0.38 V vs SCE). A platinum-basket working electrode was employed for coulometry. The low solubility of $[Ag(9S3)Cl]$ and $[Ag(12S3)_2](CF_3SO_3)$ in $MeNO_2$ and MeCN precluded electrochemical measurements.

Preparation of Compounds. All solvents were distilled under nitrogen from appropriate drying agents and stored over molecular sieves. The ligands 9S3,[8] 12S3,[9] and 18S6[10] were prepared by published methods. Silver(I) trifluoromethanesulfonate (benzene solvate), $Ag(CF_3SO_3)\cdot{}^1/_2(C_6H_6)$, was prepared by reaction of Ag_2O and CF_3SO_3H in methanol, followed by removal of the methanol in vacuo and recrystallization of the residue from benzene. Silver chloride was prepared immediately before use by combining aqueous solutions of silver acetate and sodium chloride.

$[Ag(9S3)_2](CF_3SO_3)$. To a solution of 9S3 (242 mg, 1.34 mmol) in methanol (5 mL) was added $Ag(CF_3SO_3)\cdot{}^1/_2(C_6H_6)$ (205 mg, 0.69 mmol). The solution was stirred for 2 h at room temperature and the resulting white precipitate collected by filtration and dried in vacuo. Yield: 188 mg, 78%. Anal. Calcd for $C_{13}H_{24}S_7O_3F_3Ag$: C, 25.3; H, 3.9. Found: C, 25.5; H, 3.8. IR (Nujol mull, cm^{-1}): 1400 (w), 1377 (w), 1306 (m), 1282 (s), 1260 (s), 1221 (m), 1187 (w), 1149 (s), 1030 (s), 922 (m), 879 (m), 836 (w), 821 (m), 752 (w), 667 (m), 634 (s), 613 (m). ^{1}H NMR (CD_3NO_2, δ vs Me_4Si): 3.00 (s). Conductivity in nitromethane: $\Lambda_M = 87\ (2)\ \Omega^{-1}\ cm^2\ mol^{-1}$.[11] Crystals suitable for diffraction studies were grown from methanol at 0 °C.

$[Ag(9S3)](CF_3SO_3)$. To a solution of 9S3 (182 mg, 1.01 mmol) in methanol (5 mL) was added $Ag(CF_3SO_3)\cdot{}^1/_2(C_6H_6)$ (300 mg, 1.01 mmol), and the solution was stirred for 1 h. The fine white needles of the 1:1 complex were collected, washed with methanol and diethyl ether, and dried in vacuo. Anal. Calcd for $C_7H_{12}F_3O_3S_4Ag$: C, 19.2; H, 2.8. Found: C, 19.3; H, 3.0. Conductivity in nitromethane $\Lambda_M = 92\ (2)\ \Omega^{-1}\ cm^2\ mol^{-1}$.

$[Ag(9S3)Cl]$. Method i. Silver chloride (40.5 mg, 0.28 mmol) was suspended in methanol and 9S3 (100 mg, 0.55 mmol) added. The suspension was refluxed for 1 h and the resulting solution filtered to remove traces of metallic silver. White crystals formed on cooling and were collected by filtration and dried in vacuo. Yield: 19 mg, 21%. Anal. Calcd for $C_6H_{12}S_3ClAg$: C, 22.3; H, 3.7. Found: C, 22.4; H, 3.9. IR (Nujol mull, cm^{-1}): 1447 (s), 1423 (w), 1408 (s), 1398 (s), 1377 (m), 1308 (m), 1293 (s), 1283 (m), 1189 (m), 1182 (w), 1158 (w), 1140 (m), 926 (s), 890 (s), 832 (m), 820 (s), 814 (s), 722 (w), 667 (m), 607 (m).

Method ii. To a methanolic solution of $[Ag(9S3)_2](CF_3SO_3)$ was added either a methanol solution of benzyltriethylammonium chloride (in excess) or one drop of concentrated hydrochloric acid. After a few seconds the product crystallized as colorless plates and was collected. Conductivity measurements on nitromethane solutions showed that the compound is a nonelectrolyte. Slow cooling of a hot methanol solution of the compound gave crystals suitable for X-ray diffraction studies.

$[Ag(18S6)Br]$. Hexathia-18-crown-6 (100 mg, 0.275 mmol) and silver nitrate (46 mg, 0.275 mmol) were dissolved in warm acetonitrile (8 mL). Colorless needles of $[Ag(18S6)NO_3]$ formed on standing and were isolated by filtration. Anal. Calcd for $C_{12}H_{24}S_6AgNO_3$: C, 27.2; H, 4.6; N, 2.6. Found: C, 27.1; H, 4.6; N, 2.7. Dissolution of the nitrate salt in warm acetonitrile containing an excess of tetrabutylammonium bromide gave diffraction-quality colorless hexagonal prismatic crystals of $[Ag(18S6)Br]$ on standing overnight. Anal. Calcd for $C_{12}H_{24}S_6AgBr$: C, 26.28; H, 4.41; S, 35.07; Br, 14.57. Found: C, 26.37; H, 4.42; S, 34.85; Br, 14.31.

$[Ag(12S3)_2](CF_3SO_3)$. Mixture of methanolic solutions of $Ag(CF_3SO_3)\cdot{}^1/_2C_6H_6$ (103.9 mg, 0.35 mmol) and 12S3 (161.3 mg, 0.73 mmol) immediately yielded a white precipitate. After the mixture was stirred for 1 h, the product was collected and dried. Yield: 180.1 mg, 73%. Analysis reveals that the metal:ligand ratio varies in the range 1.5–2.0 depending on the reaction conditions. IR (Nujol mull, cm^{-1}): 1274 (s), 1223 (s), 1144 (s), 1031 (s), 957 (m), 840 (m), 796 (m), 755 (m), 709 (m), 638 (s).

$[Ag(12S3)](CF_3SO_3)\cdot MeCN$. Recrystallization of $[Ag(12S3)_2](CF_3SO_3)$ from acetonitrile yielded colorless prisms of the compound. Anal. Calcd for $C_{12}H_{21}F_3NO_3S_4Ag$: C, 27.7; H, 4.1; N, 2.7. Found: C, 27.8; H, 4.1; N, 2.7. Conductivity measurements in acetonitrile are consistent with a 1:1 electrolyte.

None of the compounds exhibited obvious sensitivity to light.

Chemical Oxidation of $[Ag(9S3)_2](CF_3SO_3)$. The unstable blue $[Ag(9S3)_2]^{2+}$ ion results from (i) addition of ceric ammonium nitrate (22.1 mg, 0.040 mmol) to $[Ag(9S3)_2](CF_3SO_3)$ (23.0 mg, 0.037 mmol) in methanol (5 mL), (ii) addition of excess lead(IV) oxide to a suspension of the complex in 0.1 M H_2SO_4, or (iii) addition of $NOBF_4$ (16.0 mg, 0.14 mmol) to $[Ag(9S3)_2]$(triflate) (76.2 mg, 0.14 mmol) in MeCN (4 mL). The resulting deep blue solutions bleach rapidly at room temperature, but are stable at −70 °C. Attempts to isolate pure samples of $[Ag(9S3)_2]^{2+}$ have been unsuccessful.

X-ray Crystallography

General Procedures. Details of the crystal structure determinations are summarized in Table I. A suitable crystal was sealed in a Lindemann capillary and centered on an Enraf-Nonius CAD4 or Syntex R3 automatic diffractometer. Graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å) was used for $[Ag(9S3)_2](CF_3SO_3)$, $[Ag(18S6)Br]$, and $[Ag(12S3)](CF_3SO_3)\cdot MeCN$, but Cu K$\alpha$ radiation (λ = 1.5418 Å) was used for $[Ag(9S3)Cl]$. Unit cell parameters and an orientation matrix were obtained from least-squares fitting of the setting angles of 25 re-

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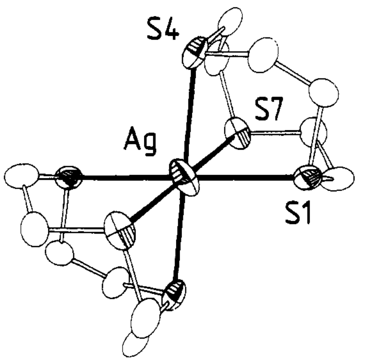

Figure 2. ORTEP view of the $[Ag(9S3)_2]^+$ cation, showing thermal ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity. Atomic numbering in the ligand rings follows IUPAC nomenclature (i.e. atoms are numbered sequentially around the ring; S1, C2, C3, S4, etc.).

Table II. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^4$) for $[Ag(9S3)_2](CF_3SO_3)$

atom	*x*/*a*	*y*/*b*	*z*/*c*	U^a
Ag	0	0	0	759
S1	−1587 (2)	1593 (1)	616.9 (6)	484
S4	1313 (2)	−361 (1)	1039.9 (7)	515
S7	−2563 (2)	−1180 (1)	468.2 (6)	507
S10	477 (3)	4491 (2)	2500	478
C2	−776 (8)	1432 (4)	1329 (2)	465
C3	990 (8)	955 (5)	1356 (3)	568
C5	−236 (7)	−1183 (4)	1399 (3)	513
C6	−1322 (8)	−1861 (4)	1004 (3)	588
C8	−3746 (6)	−198 (5)	871 (3)	480
C9	−3658 (7)	950 (5)	652 (3)	567
C10	−611 (17)	5782 (8)	2500	644
F11	−2297 (9)	5647 (6)	2500	944
F12	−217 (8)	6360 (3)	2955 (2)	897
O11	2235 (8)	4846 (6)	2500	780
O12	−90 (6)	4005 (3)	3011 (2)	602

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $[Ag(9S3)_2](CF_3SO_3)^a$

Ag–S1	2.753 (1)	Ag–S4	2.696 (2)
Ag–S7	2.727 (2)		
S1–C2	1.806 (5)	S1–C9	1.819 (6)
S4–C3	1.811 (6)	S4–C5	1.801 (6)
S7–C6	1.807 (7)	S7–C8	1.803 (5)
C2–C3	1.513 (8)	C5–C6	1.519 (8)
C8–C9	1.514 (8)		
S4–Ag–S1′	100.70 (4)	S4–Ag–S1	79.30 (4)
S7–Ag–S1	80.50 (3)	S7–Ag–S1′	99.50 (3)
S7–Ag–S4	80.14 (3)	S7–Ag–S4′	99.86 (3)

[a] Symmetry for a primed atom: −*x*, −*y*, −*z*.

Table IV. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for [Ag(9S3)Cl]

atom	*x*/*a*	*y*/*b*	*z*/*c*	U^a
Ag	119.2 (9)	1667.9 (7)	3702.1 (2)	386
Cl	1546.2 (9)	3507 (2)	3889.2 (6)	338
S1	−1032.0 (9)	809 (2)	4564.6 (5)	270
S4	−99 (1)	−2062 (2)	3400.0 (6)	330
S7	−1427 (1)	2207 (2)	3063.3 (5)	283
C2	−1213 (5)	−1854 (9)	4458 (3)	331
C3	−436 (5)	−2945 (10)	4131 (3)	389
C5	−1208 (5)	−2018 (9)	2972 (2)	328
C6	−1404 (4)	−79 (10)	2629 (2)	315
C8	−2350 (4)	1631 (9)	3586 (2)	306
C9	−2105 (4)	1934 (11)	4243 (3)	343

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Selected Bond Lengths (Å) and Angles (deg) for [Ag(9S3)Cl]

Ag–Cl	2.389 (1)	Ag–S1	2.618 (1)
Ag–S4	2.598 (1)	Ag–S7	2.599 (1)
S1–C2	1.813 (6)	S1–C9	1.822 (6)
S4–C5	1.813 (6)	S4–C3	1.809 (7)
S7–C6	1.809 (6)	S7–C8	1.816 (6)
C2–C3	1.52 (1)	C5–C6	1.525 (8)
C8–C9	1.506 (8)		
S1–Ag–Cl	121.66 (5)	S4–Ag–Cl	129.20 (5)
S7–Ag–Cl	135.82 (5)	S4–Ag–S1	84.71 (5)
S7–Ag–S4	84.24 (4)	S7–Ag–S1	84.33 (4)

flections collected by an automatic search routine. Data were corrected for Lorentz and polarization effects. Three standard reflections measured every hour showed no decay. An empirical absorption correction was applied. The structures were all solved by routine Patterson and Fourier techniques. In all cases, most hydrogen atoms were apparent on difference maps after isotropic refinement of the rest of the structure, but all were included in calculated positions. Full-matrix least-squares refinement was continued with anisotropic temperature factors for all non-hydrogen atoms and group isotropic temperature factors for H atoms (except for [Ag(18S6)Br], where H atom temperature factors were fixed at $^6/_5$ times that of the bonded C atom). Calculations were performed on a VAX 11/750 computer with the CRYSTALS suite of crystallographic programs[12] or a Nova 3 computer with SHELX. Atomic scattering factors were taken from the usual source.[13] Unusual features of the structures are outlined below.

$[Ag(9S3)_2](CF_3SO_3)$. The large anisotropic temperature factors associated with the trifluoromethanesulfonate ion (which is on a crystallographic mirror plane) suggest slight disorder. In addition, the largest peak in the final difference map appeared close to O12 of that ion. However, attempts to model the disorder failed to improve either *R* or the difference map.

Thermal parameters on the Ag ion exceeded those of all other atoms in the cation and yield a thermal ellipsoid elongated parallel to the ligand S3 planes (Figure 2). This elongation may reflect mobility of the silver ion in the plane of the ligand "sandwich"; alternatively, it may result from inadequate correction for absorption. None of the other crystal structures showed this effect.

[Ag(9S3)Cl]. The use of Cu Kα radiation evidently denigrated the quality of the data set. The large values of R_{merge}, *R*, and R_w originate from absorption of the Cu Kα radiation by the silver atom (μ = 231 cm^{-1}). The highest peak in the final difference map was next to Ag.

[Ag(18S6)Br]. The unit cell parameters approach those of a monoclinic cell, although not sufficiently closely to introduce any ambiguity in the structure. Final positional parameters did not indicate the presence of higher symmetry.

$[Ag(12S3)](CF_3SO_3)\cdot MeCN$ shows slight disorder in the coordinated anion and the solvent, as evidenced by the large thermal parameters, especially of F3 and N. No attempt was made to model it.

Results

Descriptions of the Structures. $[Ag(9S3)_2](CF_3SO_3)$. In the centrosymmetric $[Ag(9S3)_2]^+$ cation (Figure 2; Tables II and III), two tridentate 9S3 ligands sandwich the silver ion to yield a six-coordinate complex. The Ag coordination sphere deviates from octahedral geometry through trigonal elongation: nonchelating S–Ag–S angles (average 100°) exceed chelating ones (average 80°) by 20°.

Silver–sulfur distances are longer than those in most silver–thioether complexes. Distances here range from 2.696 (2) to 2.753 (1) Å (average 2.72 Å), compared with the more typical value of approximately 2.60 Å. This dilation of the coordination sphere contrasts with the usual compression generated by 9S3 in its transition-metal complexes. In $[Ag(9S3)_2]^+$, however, the long Ag–S distances reflect the high coordination number, since most Ag–thioether complexes exhibit two-, three-, or four-coordination.

[Ag(9S3)Cl] contains a four-coordinate silver ion in a distorted tetrahedral coordination sphere (Figure 3; Tables IV and V).

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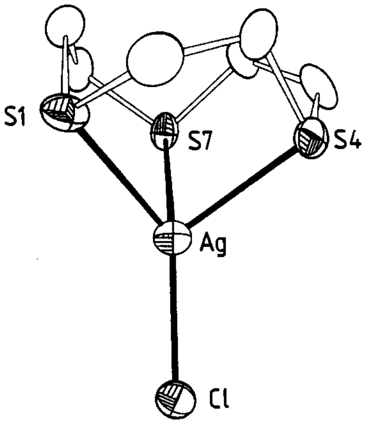

Figure 3. ORTEP view of [Ag(9S3)Cl], showing thermal ellipsoids at the 50% probability level. hydrogen atoms are omitted for clarity. Atomic numbering is as in Figure 1.

Table VI. Torsional Angles (deg) for $[Ag(9S3)_2](CF_3SO_3)$, [Ag(9S3)Cl], and Free 9S3

angle	$[Ag(9S3)_2](CF_3SO_3)$	[Ag(9S3)Cl]	free 9S3
C9–S1–C2–C3	129.0 (1)	125.6 (1)	131.1 (1)
S1–C2–C3–S4	−58.6 (1)	−54.9 (1)	−58.6 (1)
C2–C3–S4–C5	−55.7 (1)	−54.4 (1)	−55.0 (1)
C3–S4–C5–C6	130.6 (1)	131.2 (1)	131.1 (1)
S4–C5–C6–S7	−58.5 (1)	−57.9 (1)	−58.6 (1)
C5–C6–S7–C8	−53.3 (1)	−58.0 (1)	−55.0 (1)
C6–S7–C8–C9	129.0 (1)	128.0 (1)	131.1 (1)
S7–C8–C9–S1	−60.2 (1)	−51.5 (1)	−58.6 (1)
C8–C9–S1–C2	−53.7 (1)	−61.4 (1)	−55.0 (1)

Table VII. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for [Ag(18S6)Br]

atom	x/a	y/b	z/c	U^a
Ag	1625 (1)	7529 (1)	4543 (1)	43
Br	2530 (1)	5155 (1)	4903 (1)	46
S1a	166 (1)	8914 (1)	6123 (1)	41
S4a	−825 (1)	6875 (1)	2396 (1)	37
S7a	−1034 (2)	2917 (1)	240 (1)	62
S1b	3702 (1)	8853 (1)	4945 (1)	34
S4b	4367 (1)	5347 (1)	1302 (1)	47
S7b	3497 (1)	1045 (1)	772 (1)	55
C2a	−1468 (4)	7842 (4)	4831 (4)	43
C3a	−1954 (4)	7818 (4)	3347 (4)	44
C5a	−1183 (4)	5046 (3)	2008 (4)	37
C6a	−499 (5)	4063 (4)	1016 (4)	49
C8a	−80 (5)	1674 (4)	1719 (4)	54
C9a	−933 (4)	1900 (4)	2572 (4)	47
C2b	4116 (4)	7830 (4)	3388 (4)	39
C3b	4050 (4)	6238 (4)	2918 (4)	42
C5b	4654 (4)	3554 (4)	1206 (4)	47
C6b	3417 (4)	2944 (4)	1221 (4)	44
C8b	5010 (4)	909 (4)	2281 (4)	49
C9b	4794 (4)	1518 (4)	3656 (4)	40

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

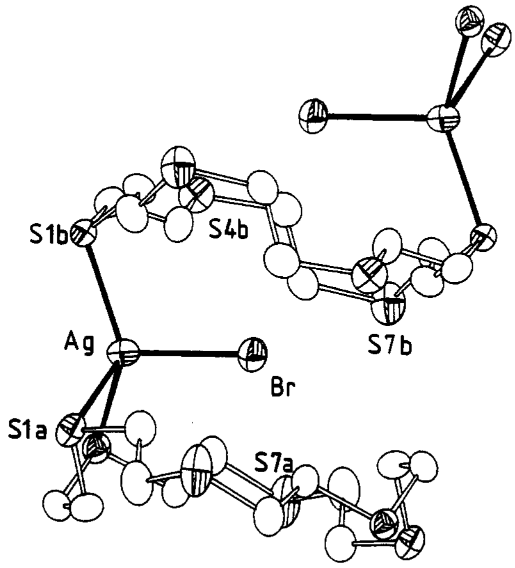

Figure 4. ORTEP view of [Ag(18S6)Br], showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Atomic numbering is as in Figure 1.

Table VIII. Selected Bond Lengths (Å) and Angles (deg) for $[Ag(18S6)Br]^a$

Ag–Br	2.636 (1)	Ag–S1a	2.636 (1)
Ag–S4a	2.571 (1)	Ag–S1b	2.514 (1)
S1a–C9a′	1.839 (5)	S1a–C2a	1.820 (3)
S4a–C3a	1.813 (5)	S4a–C5a	1.824 (4)
S7a–C8a	1.806 (5)	S7a–C6a	1.819 (4)
S1b–C2b	1.815 (4)	S1b–C9b″	1.814 (4)
S4b–C5b	1.807 (5)	S4b–C3b	1.805 (5)
S7b–C8b	1.794 (4)	S7b–C6b	1.815 (4)
C2a–C3a	1.519 (7)	C5a–C6a	1.504 (6)
C8a–C9a	1.496 (8)	C3b–C2b	1.510 (5)
C6b–C5b	1.530 (7)	C9b–C8b	1.506 (6)
Br–Ag–S1a	108.7 (1)	Br–Ag–S4a	105.6 (1)
S1a–Ag–S4a	85.7 (1)	Br–Ag–S1b	109.3 (1)
S1a–Ag–S1b	116.9 (1)	S4a–Ag–S1b	127.9 (1)

[a] Symmetry for a primed atom: $-x$, $1-y$, $1-z$. Symmetry for a double-primed atom: $1-x$, $1-y$, $1-z$.

Table IX. Torsional Angles (deg) for $[Ag(18S6)Br]^a$

C9a′–S1a–C2a–C3a	−154.0 (1)
S1a–C2a–C3a–S4a	68.4 (1)
C2a–C3a–S4a–C5a	70.0 (1)
C3a–S4a–C5a–C6a	171.7 (1)
S4a–C5a–C6a–S7a	−168.7 (1)
C5a–C6a–S7a–C8a	74.2 (1)
C6a–S7a–C8a–C9a′	−90.2 (1)
S7a–C8a–C9a–S1a′	169.3 (1)
C8a–C9a–S1a′–C2a′	−67.9 (1)
C9b″–S1b–C2b–C3b	67.0 (1)
S1b–C2b–C3b–S4b	176.3 (1)
C2b–C3b–S4b–C5b	167.1 (1)
C3b–S4b–C5b–C6b	55.5 (1)
S4b–C5b–C6b–S7b	168.4 (1)
C5b–C6b–S7b–C8b	−68.8 (1)
C6b–S7b–C8b–C9b″	−68.8 (1)
S7b–C8b–C9b″–S1b″	−173.4 (1)
C8b–C9b″–S1b″–C2b″	−172.9 (1)

[a] Symmetry for a primed atom: $-x$, $1-y$, $1-z$. Symmetry for a double-primed atom: $1-x$, $1-y$, $1-z$.

Bond angles at silver reflect a distortion from tetrahedral geometry, since chelating S–Ag–S angles average 84°, while S–Ag–Cl angles average 129°. The distortion results from the small bite of 9S3, which as a tridentate ligand cannot simultaneously afford optimal Ag–S distances and tetrahedral bond angles. (Bond angles at Ag in [Ag(9S3)Cl] exceed the corresponding ones in $[Ag(9S3)_2]^+$ by only ca. 4°.) Curiously, the Ag–Cl vector is not perpendicular to the S_3 plane; S–Ag–Cl angles vary from 121.7 (5) to 135.8 (5)°.[14] Silver–sulfur distances range from 2.598 (1) to 2.618 (1) Å and average 0.1 Å shorter than those in $[Ag(9S3)_2]^+$. The contrast between these typical Ag–S distances and the long ones in $[Ag(9S3)_2]^+$ reflects the higher coordination number in the bis complex.

[Ag(18S6)Br] crystallizes as a one-dimensional polymer (Figure 4, Tables VII–IX) with AgBr units interleaving stacks of roughly planar crowns. The Ag coordination sphere (Figure 5) comprises a halide ion, two thioethers from one ligand molecule, and one thioether from another ligand molecule. Together they give a

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(14) Intermolecular distances contain no unexpectedly short contacts, nor do Ag–S distances vary correspondingly.

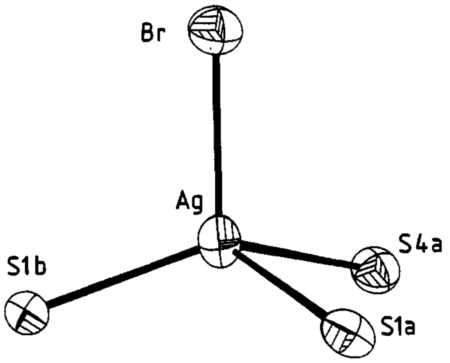

Figure 5. ORTEP view of the Ag(I) coordination sphere in [Ag(18S6)Br], showing thermal ellipsoids at the 50% probability level.

Table X. Atomic Coordinates (×10^4) and Temperature Factors (Å^2 × 10^4) for [Ag(12S3)](CF_3SO_3)·MeCN

atom	*x/a*	*y/b*	*z/c*	*U*[a]
Ag	585.5 (6)	5695.8 (3)	6255.0 (3)	393
S1	−1101 (2)	7038 (1)	6606 (1)	372
S5	−2689 (2)	9718 (1)	8147 (1)	378
S9	−3298 (2)	9115 (1)	5250.9 (9)	333
S10	−2129 (2)	4351 (1)	4969 (1)	508
F1	−4204 (8)	3436 (5)	5802 (4)	868
F2	−4094 (8)	3044 (5)	4568 (4)	900
F3	−2368 (10)	2623 (5)	5400 (8)	1186
O1	−1366 (9)	4555 (5)	5730 (4)	793
O2	−1141 (8)	4084 (6)	4314 (5)	866
O3	−3289 (10)	5011 (5)	4731 (6)	996
C2	−2117 (10)	6891 (5)	7596 (4)	439
C3	−2947 (9)	7778 (5)	7859 (5)	445
C4	−1800 (8)	8555 (5)	8060 (4)	423
C6	−3160 (9)	10010 (5)	7077 (4)	431
C7	1802 (9)	10136 (5)	6493 (4)	453
C8	−2365 (9)	10194 (6)	5599 (4)	448
C10	−1649 (8)	8371 (5)	5026 (4)	424
C11	−2137 (9)	7350 (6)	5028 (5)	425
C12	−2694 (8)	6984 (5)	5866 (5)	439
C100	−3199 (10)	3310 (6)	5210 (6)	575
C200	2135 (13)	1915 (9)	2204 (6)	685
C201	2374 (12)	915 (8)	2282 (7)	791
N1	1944 (16)	2678 (8)	2129 (7)	1085

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table XI. Selected Bond Distances (Å) and Angles (deg) for [Ag(12S3)](CF_3SO_3)·MeCN[a]

Ag–S1	2.463 (2)	Ag–S5″	2.477 (2)
Ag–S9″	2.621 (2)	Ag–O1	2.483 (6)
S1–C2	1.829 (7)	S1–C12	1.817 (7)
S5–C4	1.827 (7)	S5–C6	1.818 (7)
S9–C8	1.819 (8)	S9–C10	1.806 (7)
C2–C3	1.51 (1)	C3–C4	1.52 (1)
C6–C7	1.51 (1)	C7–C8	1.52 (1)
C10–C11	1.51 (1)	C11–C12	1.52 (1)
S5′–Ag–S1	140.92 (6)	S9″–Ag–S1	110.42 (5)
S9″–Ag–S5	98.58 (5)	O1–Ag–S1	100.7 (2)
O1–Ag–S5′	105.0 (2)	O1–Ag–S9″	90.0 (2)

[a] Symmetry for a primed atom: $-x, y - {}^1/_2, {}^3/_2 - z$. Symmetry for a double-primed atom: ${}^1/_2 + x, {}^3/_2 - y, 1 - z$.

Table XII. Torsional Angles (deg) for [Ag(12S3)](CF_3SO_3)·MeCN and Free 12S3

angle	[Ag(12S3)](CF_3SO_3)·MeCN	free 12S3
C12–S1–C2–C3	−76	−65.0
S1–C2–C3–C4	−67	−64.2
C2–C3–C4–S5	166	167.6
C3–C4–S5–C6	−72	−70.8
C4–S5–C6–C7	−65	−76.0
S5–C6–C7–C8	169	162.5
C6–C7–C8–S9	−64	−65.9
C7–C8–S9–C10	−79	−66.1
C8–S9–C10–C11	159	156.6
S9–C10–C11–C12	−64	−75.4
C10–C11–C12–S1	−63	−67.7
C11–C12–S1–C2	165	172.6

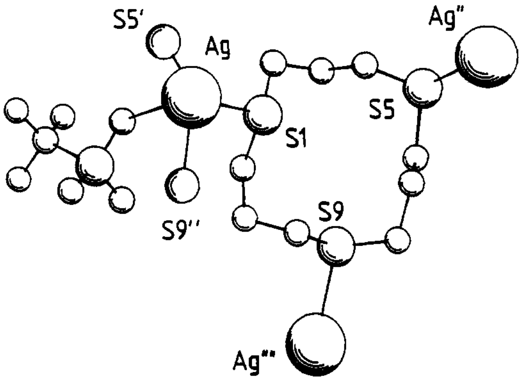

Figure 6. CHEMGRAF view of [Ag(12S3)](CF_3SO_3)·MeCN. The solvent and hydrogen atoms are omitted for clarity. Atomic numbering in the ligand ring follows IUPAC nomenclature (i.e. S1, C2, C3, C4, S5, etc.).

distorted-tetrahedral geometry about the metal ion. The compound contains two independent types of centrosymmetric bridging 18S6 molecules that alternate in the stack. One type acts as a bidentate chelate to each of two AgBr units, while the other binds as a monodentate ligand to each of two AgBr units.

[Ag(12S3)](CF_3SO_3)·MeCN displays two noteworthy features. First, Ag(I) coordinates to $CF_3SO_3^-$ in preference to MeCN (Ag–N = 3.44 Å). The resulting Ag coordination sphere consists of a triflate anion and three thioether groups. Second, these three thioether groups (Ag–S = 2.463 (2)–2.621 (2) Å; Tables X, XI) do not come from a single ligand (cf. $[Ru(12S3)_2]^{2+}$[15,16] and $[Ni(12S3)_2]^{2+}$[17]). Instead, each Ag(I) coordinates with one thioether from each of three symmetry-related ligands that retain the conformation of free 12S3[18] (Table XII). Each ligand molecule in turn coordinates to three separate Ag(I) ions to yield a polymeric network structure (Figure 6).

Synthesis of Complexes. Despite their apparent similarity, 9S3 aand 12S3 differ qualitatively in their coordinative behavior toward Ag(I). Owing to its uniquely favorable conformation,[7] 9S3 strongly tends to coordinate in a tridentate fashion, which usually results in simple discrete complexes. By contrast, because of its especially unfavorable conformation (all three S atoms exodentate),[9,18] free 12S3 often forms oligomers instead of discrete complexes.

9S3 Complexes. Reaction of Ag(I) with 2 equiv of 9S3 in MeOH yields $[Ag(9S3)_2](CF_3SO_3)$.[3] This compound behaves as a 1:1 electrolyte in $MeNO_2$, and hence it probably maintains the solid-state structure in solution.

Reaction of a single equivalent of 9S3 (with $Ag(CF_3SO_3)\cdot{}^1/_2(C_6H_6)$) gives [Ag(9S3)]($CF_3SO_3$). Structurally this compound could resemble [Ag(9S3)Cl] (with Cl^- coordinating in place of $CF_3SO_3^-$). Alternatively, it could contain a condensed trimeric thioether-bridged species (in conjunction with noncoordinated $CF_3SO_3^-$ anions), as in $[Ag_3(9S3)_3]^{3+}$.[4]

Addition of chloride salts to $[Ag(9S3)_2]^+$ in MeOH or $MeNO_2$ displaces one 9S3 ligand to yield [Ag(9S3)Cl]. This compound also results from dissolution of AgCl in a refluxing solution of 9S3 in methanol.

12S3 and 18S6 Complexes. In contrast with the 9S3 analogue, $[Ag(12S3)_2](CF_3SO_3)$ dissolves sparingly in noncoordinating solvents (e.g., MeOH, $MeNO_2$). This low solubility suggests an

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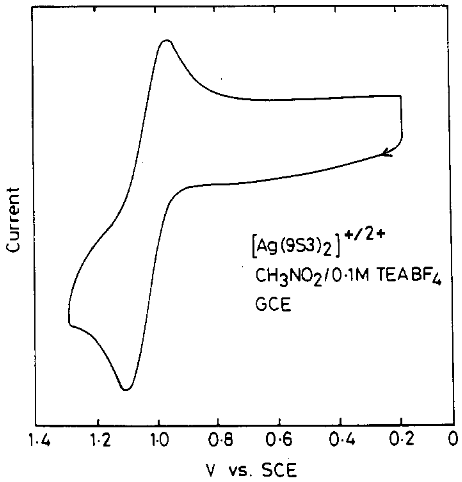

Figure 7. Cyclic voltammogram of [Ag(9S3)$_2$]$^+$ in nitromethane at a glassy-carbon electrode. Scan rate: 100 mV s^{-1}.

oligomeric structure. Its considerable solubility in MeCN presumably results from disruption of the polymeric structure to yield an ionic solution. Surprisingly, crystals obtained from these solutions do not contain coordinated MeCN; instead, it is oligomeric. The parent compound, [Ag(12S3)$_2$](CF$_3$SO$_3$), may have an analogous structure. [Ag(18S6)Br], which shows similar solubility properties, also crystallizes as an oligomer.

Electrochemistry. Of the compounds reported here, only [Ag(9S3)$_2$)]$^+$ shows essentially reversible electrochemistry. Cyclic voltammetry of [Ag(9S3)$_2$](CF$_3$SO$_3$) in MeNO$_2$ at a Pt disk reveals the [Ag(9S3)$_2$]$^{2+/+}$ process (Figure 7) at +1.10 V vs SCE (ΔE_p = 106 mV; scan rate = 500 mV s^{-1}). At room temperature i^c_p/i^a_p increases from unity at 500 mV s^{-1} with decreasing scan rate. Lower temperatures slow the rapid chemical reaction of the oxidized species; at −20 °C i^c_p/i^a_p approaches unity for scan rates greater than 20 mV s^{-1}.

Electrolysis in MeNO$_2$ at +1.3 V vs SCE gives a deep blue solution of [Ag(9S3)$_2$]$^{2+}$ that decolorizes rapidly (1 min) following electrolysis. Coulometry shows that the process involves transfer of one electron (n = 0.9). Chemical oxidation similarly yields deep blue solutions (λ_{max} 366 nm; $\epsilon = 7.4 \times 10^4$ mol^{-1} dm^3 cm^{-1}, estimated by extrapolation to t = 0) that bleach within a few seconds at room temperature but are stable at −70 °C. Bleaching probably results from oxidation of a thioether group to the sulfoxide in the presence of adventitious water (as in thioether complexes of Cu(II)) in an EC process.

EPR spectroscopy of the chemically oxidized material confirms formation of a paramagnetic product. At 149 K this solution exhibits an isotropic EPR signal (g = 2.03) without resolved hyperfine splitting. The absence of ^{107}Ag or ^{109}Ag hyperfine splitting (^{107}Ag, $I = {}^1/_2$, 51.4%; ^{109}Ag, $I = {}^1/_2$, 48.6%) probably results from the small nuclear magnetic moments of these nuclides and the substantial line width of the signal (50 G; 1 G = 10^{-4} T).

These observations indicate formation of [Ag(9S3)$_2$]$^{2+}$, although they do not define the location of the odd electron. Note, however, that Ce(IV) oxidizes neither free 9S3 nor Ag(I) under the same conditions. Furthermore, at a Pt electrode, 9S3 oxidizes irreversibly at +1.37 V vs SCE (cf. [Ag(9S3)$_2$]$^{2+/+}$ where E_f = +1.10 V vs SCE) to an EPR-silent product. Coordination should make 9S3 *more* difficult to oxidize, while it may increase or decrease the Ag(II/I) potential, depending on which oxidation states binds more strongly to 9S3.

Discussion

Attainment of six-coordination in [Ag(9S3)$_2$]$^+$ contrasts with the ubiquity of linear or tetrahedral coordination in Ag(I) complexes.[19] Examples of both occur among thioether complexes.[20,21] Some multidentate macrocyclic ligands enforce five- or six-coordination on Ag(I), and some of these ligands include thioether donors.[22-24] In these complexes, however, and also in many of those with monodentate ligands,[25,26] Ag–L distances within the coordination sphere vary widely.

In contrast, [Ag(9S3)$_2$]$^+$ displays a regular coordination sphere with idealized trigonal-antiprismatic geometry. Comparison of [Ag(9S3)$_2$]$^+$ with [Ag$_2$(1,3,5-trithiane)$_5$]$^{2+}$ [27] and Ag(1,3,5-trithiane)X (X = NO$_3$, ClO$_4$)[28] emphasizes this point. The trithiane complexes contain both four- and five-coordinate Ag(I) with Ag–S distances ranging from 2.519 (3) to 2.924 (3) Å.

[Ag(9S3)Cl] adopts a structure more typical of Ag(I) complexes. 9S3 coordinates to the AgCl unit in a tridentate fashion to yield a four-coordinate complex in which the Ag–S distances vary little. The small S–Ag–S angles (average 84°) indicate that 9S3 accommodates a tetrahedral face of Ag(I) only through the stereochemical plasticity of the metal, rather than conformational flexibility of the ligand. The AgS$_3$Cl coordination sphere elongates along the idealized C_3 axis; this contrasts with the compression in [Ag(PPh$_3$)$_3$Cl] (where P–Ag–P angles average 115° as a result of steric repulsion between the bulky PPh$_3$ ligands).[29]

Coordination of 9S3 to Ag(I) necessitates negligible change in the conformation (Table VI). In fact, ligand torsional angles in [Ag(9S3)$_2$]$^+$ and [Ag(9S3)Cl] match those of free 9S3 more closely than in any other complex reported to date.[30] This improved "fit" between metal ion and ligand results from both the large ionic radius and the weak stereochemical preferences of Ag(I). (These manifest themselves in the unusually large trigonal elongation of [Ag(9S3)$_2$]$^+$.) Together these factors allow the Ag(I) ion to lie at the "focus" of the sulfur lone pairs without distortion of the ligand. In transition-metal complexes, on the other hand, chelation of 9S3 requires slight distortion of the metal ion stereochemistry and/or the ligand conformation. Thus the excellent stereochemical match between Ag$^+$ and 9S3 promotes six-coordination.

Because of its conformational predisposition to chelation, 9S3 forms more stable complexes than other crown thioethers. This thermodynamic stability, however, does not preclude kinetic lability: ^{1}H NMR reveals only a singlet for this fluxional complex (300 K, CD$_3$NO$_2$ solution), unlike the more complex spectra of nonlabile complexes.[15,30c]

In contrast to 9S3, 18S6 and 12S3 display little tendency to chelate Ag(I). The major structural differences between what might naively be considered homologous compounds reflects the role of ligand conformation in determining coordination chemistry. Thus while the endodentate conformation of 9S3 dictates tridentate chelation of Ag(I), the square conformation of 12S3 (in which none of the thioether donors are endodentate) virtually precludes it. Similarly, the three consecutive thioethers in [Ag(18S6)Br] fail to chelate to a single AgX unit.[31] The driving force for

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chelation in [Ag(9S3)Cl] originates in the unique conformation of the nine-membered ring.

Strong coordination by 9S3 qualitatively influences the electrochemical behavior of $[Ag(9S3)_2]^+$. First, by promoting six-coordination, it presumably generates high electron density on the metal and thereby promotes oxidation to $[Ag(9S3)_2]^{2+}$ at a relatively low potential.

Second, it improves the reversibility of the $[Ag(9S3)_2]^{2+/+}$ couple. Typically ligands form stable complexes either with Ag(I) or with Ag(II), but not both. For example, the stable $[Ag(cyclam)]^{2+}$ cation[32] (cyclam = 1,4,8,11-tetraazacyclotetradecane) disproportionates on reduction.[33] Larger N_4 macrocycles form stable complexes with Ag(I) but not Ag(II).[34] Irreversibility results in either case, since only half of the couple exists in solution. Thioethers thermodynamically stabilize lower oxidation states of metal ions by binding more strongly to them than to those in higher oxidation states.[35] Oxidation therefore decrements the stability of a thioether complex. Complexes of 9S3, however, are so stable that even the more weakly bound oxidized form still has sufficient stability to resist ligand substitution by solvent molecules. Electrochemical reversibility results, since both oxidized and reduced forms can exist in solution.

Conclusions

Coordination of conformationally favorable crown thioethers imposes not only different coordination behavior on Ag(I)—in this case six- instead of four-coordination—but also different electrochemistry. The facile oxidation of $[Ag9S3)_2]^+$ apparently results from the great stability of 9S3 complexes; as a consequence of this stability, oxidation to the dication yields a reasonably stable complex that can be observed by cyclic voltammetry. These results underscore once again the singular attributes conferred on 9S3 by its conformation, which uniquely suits it for chelation. In a broader context, they demonstrate the importance of conformational considerations to ligand design.

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Registry No. $[Ag(9S3)_2](CF_3SO_3)$, 110922-45-7; $[Ag(9S3)](CF_3SO_3)$, 110899-85-9; [Ag(9S3)Cl], 122539-96-2; [Ag(18S6)Br], 122539-99-5; $[Ag(18S6)NO_3]$, 122566-64-7; $[Ag(12S3)](CF_3SO_3)$, 122539-98-4; $[Ag(12S3)](CF_3O_3)\cdot MeCN$, 122540-01-6; $[Ag(9S3)_2]^{2+}$, 110899-86-0.

Supplementary Material Available: Tables containing full crystallographic data, bond distances and angles, anisotropic thermal parameters, hydrogen atomic coordinates, and torsional angles (17 pages); tables of structure factors (60 pages). Ordering information is given on any current masthead page.

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Notes

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Formation of the Metal–Sulfide Aggregate $[W_3S_{10}]^{2-}$ through a Novel Balanced Intramolecular Condensation Redox Process with Principal Relevance to the Formation of Amorphous Metal Sulfides like WS_3

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Although the formation of isopoly anions by protonation of oxoanions of the transition metals has been studied in numerous investigations, little is known about corresponding reproducible stoichiometric reactions of thioanions.[1,2] We have now obtained $[W_3S_{10}]^{2-}$ (**1**) with the new $[WS_5]^{2-}$ ligand in the mixed-crystal compounds $(PPh_4)_2[W_3S_{10}]_{0.7}[W_3S_9]_{0.3}\cdot DMF$ (**2**) (DMF = *N*,*N*-dimethylformamide) and $((PPh_3)_2N)_2[W_3S_{10}]_{0.3}[W_3S_9]_{0.7}\cdot {}^1/_2CH_2Cl_2$ (**3**) by controlled acidification of a methanolic solution of $(NH_4)_2[WS_4]$ with gaseous HCl; **2** only forms in the presence of manganese chloride (see below).

Experimental Section

Table I. Crystal Data, Intensity Measurement, and Refinement Parameters for **2**–**4**

	2	**3**	**4**
mol wt	1614.5	1969.4	1593.5
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, pm	1158.7 (17)	1330.2 (3)	1186.3 (4)
b, pm	1525.6 (21)	1387.7 (3)	1282.4 (5)
c, pm	1847.7 (24)	2126.0 (4)	2043.5 (7)
α, deg	76.65 (10)	93.73 (2)	83.04 (3)
β, deg	72.73 (10)	95.03 (2)	88.25 (3)
γ, deg	67.46 (10)	99.18 (2)	63.74 (2)
V, pm^3	2855.2×10^6	3846.8×10^6	2766.7×10^6
Z	2	2	2
ρ_{calcd}, g·cm^{-3}	1.88	1.70	1.91
μ(Mo Kα), cm^{-1}	65.93	49.72	68.59
radiation	Mo Kα (graphite monochromator; λ = 71.069 pm)		
temp, K	294	294	294
R^a	0.086	0.086	0.078
$R_w{}^b$	0.084	0.130	0.086
g^c	0.0001	0.002	0.0002

$^a\sum||F_o| - |F_c||/\sum|F_o|$. $^b[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $^c1/w = \sigma^2(F_o) + gF_o{}^2$.

Synthesis. The products are prepared in an argon atmosphere. The solvents used were analytically pure and were dried over molecular sieves.

$(PPh_4)_2[W_3S_{10}]_{0.7}[W_3S_9]_{0.3}\cdot DMF$ (2). $MnCl_2\cdot 4H_2O$ (2.38 g, 12 mmol) is added to a solution of $(NH_4)_2[WS_4]$ (4.20 g, 12 mmol) in 1200 mL of methanol, and then gaseous HCl (7.5 L/h) is passed for 60–70 s through the solution under vigorous stirring. After 20 min a solution of PPh_4Cl (3.00 g, 8 mmol) in 40 mL of methanol is added and the mixture is stirred for 2 h. The precipitate is filtered off, washed with toluene, methanol, and ether, and dissolved in 90 mL of CH_2Cl_2/DMF (2:1). The solution is filtered, and the filtrate is carefully covered with a layer of 100 mL of *n*-hexane (in a cylindrical vessel, diameter ca. 3 cm) and kept for 6–8 days at 5–7 °C. Dark red crystals of **2** are filtered off, washed with toluene, methanol (to remove the small amount of coprecipitated yellow $(PPh_4)_2[WS_4]$), and ether, and dried in vacuum, yield 1.70 g (26%). Anal. Calcd (found): C, 37.9 (37.9); H, 2.9 (2.9); N, 0.9 (1.0); S, 19.3 (19.3). IR (CsI pellet): 527 ($\nu(WS_{cent})$, ν(S–S), and a cation band), 495 ($\nu(WS_{term})$), 465, 435 ($\nu(WS_{br})$), 320 ($\nu(W{-}S_2)$) cm^{-1}. Ra-

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