Crown Thioether Chemistry: Novel Silver(I) Complexes of 1,3-Dithiole-Annelated 1,4,7-Trithiacyclononane

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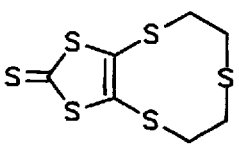
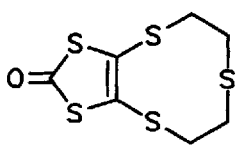
The coordination chemistry of two crown thioethers 2,5,8,10,12-pentathiabicyclo[7.3.0]dodeca-1(9)-ene-11-thione (**L**) and -11-one (**L'**) with Ag^I has been investigated by structural methods. Both thioethers act as tridentate ligands coordinating the silver ion in a trigonal fashion. In the case of **L**, the 11-thione sulfur is coordinated additionally by another silver ion, to yield a polymeric chain with a distorted-tetrahedral geometry about the metal ion. Despite differing only in its carbonyl chalcogen, **L'** forms six-coordinated, monomeric complexes.

Polythioether macrocycles have been shown to bind transition metal ions, particularly those in lower oxidation states. The number of reported structures is huge and provides a clear picture of the variety produced by subtle variations in ligand character and metal[1–3]. To date, however, there have been very few examples of crown thioether complexes containing rigid 1,2-dithioethene units[4–6].

As part of our studies on thio-crowned derivatives of 1,3-dithiole-2-thione-4,5-dithiolate (dmit) and its 2-one-analogue (dmid)[7] we have investigated the coordination chemistry of tri-thio crowns.



L



L'

$[(AgL)_n](NO_3)_n$	**1**	$[Ag(L')_2]NO_3$	**5**
$[(AgL)_n](ClO_4)_n$	**2**	$[Ag(L')_2]ClO_4$	**6**
$[(AgL)_n](BF_4)_n$	**3**	$[Ag(L')_2]BF_4$	**7**
$[(AgL)_n](PF_6)_n$	**4**	$[Ag(L')_2]PF_6$	**8**

In contrast to their well-studied, saturated analogue, 1,4,7-trithiacyclononane (**9S3**), the coordination chemistry of 2,5,8,10,12-pentathia-bicyclo[7.3.0]dodeca-1(9)-ene-11-thione (L), and 2,5,8,10,12-pentathia-bicyclo[7.3.0]dodeca-1(9)-ene-11-one (L') is still unknown. This paper describes the synthesis and characterization of silver complexes of these crown thioethers. The effect of the carbonyl chalcogen on their coordination geometry is also discussed.

Results and Discussion

Ligand **L** was originally prepared in modest yield by Jørgensen et al.[8] from disodium 1,3-dithiole-2-thione-4,5-dithiolate (Na_2dmit) and bis(2-bromoethyl)sulfide. Recently we have developed an improved general synthesis of **L** and **L'**[7].

Silver(I) Complexes of L

By reaction of one equivalent of 2,5,8,10,12-pentathiabicyclo[7.3.0]dodeca-1(9)-ene-11-thione (L) in chloroform with one equivalent of AgX ($X = NO_3^-$, ClO_4^-, BF_4^-, PF_6^-) in methanol at room temperature, silver(I) complexes **1**–**4** of general formula $[(AgL)_n]X_n$ were obtained in nearly quantitative yields. These silver complexes were isolated as yellow solids, washed with chloroform and methanol and characterized by infrared spectroscopy, ^{13}C- and ^1H-NMR spectroscopy and elemental analyses. Diffusion of isopropanol into an acetonitrile solution of the PF_6 salt **4** afforded single crytals.

X-ray analysis of complex **4** showed that $[(AgL)_n](PF_6)_n$ exists in the solid state as an infinite chain polymer. The silver ion resides in an approximately tetrahedral environment with three coordination sites occupied by facial coordination to the thioether sulfurs of one ligand and the fourth site occupied by the thione sulfur of a second ligand molecule (Figure 1, Table 1). The Ag-thione sulfur bond length of 2.425(2) Å is similar to that found for thione coordinated 4,5-dimethylthio-1,3-dithiole-2-thione [2.50(4) Å][9]. The sulfur atoms of the tridentate crown thioether coordinate silver with Ag–S(4) = 2.605(2), Ag–S(5) = 2.780(2) Å, and Ag–S(6) = 2.560(2) Å. The distorted-tetrahedral arrangement, and the bond lengths and angles, are closely parallel to those in $[Ag_3(9S3)_3]^{3+}$, the trimeric tetrahedral silver chelate of 1,4,7-trithiacyclononane[10]. Like **9S3**[11],

  0009–2940/97/0303–0425 $ 15.00+.25/0

Table 1. Selected bond lengths [Å] and angles [°] for $[(AgL)_n(PF_6)_n \cdot 1.5\ n\ CH_3CN$ **4** with estimated standard deviations (e.s.d.s) in parentheses. Symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2, y - 1/2, -z$; #2 $-x + 1/2, y + 1/2, -z$

C(1)–C(2)	1.349(8)	C(1)–S(1)	1.737(5)
C(1)–S(4)#1	1.758(6)	C(2)–S(2)	1.737(6)
C(2)–S(5)#1	1.760(6)	C(3)–S(3)	1.677(6)
C(3)–S(2)	1.708(5)	C(3)–S(1)	1.710(6)
C(4)–C(5)	1.526(10)	C(4)–S(5)	1.823(7)
C(5)–S(6)	1.813(7)	C(6)–C(7)	1.512(10)
C(6)–S(4)	1.821(7)	C(7)–S(6)	1.814(7)
S(3)–Ag	2.425(2)	S(4)–C(1)#2	1.758(6)
S(4)–Ag	2.605(2)	S(5)–C(2)#2	1.760(6)
S(5)–Ag	2.780(2)	S(6)–Ag	2.560(2)
C(2)–C(1)–S(1)	115.9(4)	C(2)–C(1)–S(4)#1	128.3(4)
S(1)–C(1)–S(4)#1	115.8(3)	C(1)–C(2)–S(2)	115.7(4)
C(1)–C(2)–S(5)#1	127.7(5)	S(2)–C(2)–S(5)#1	116.6(3)
S(3)–C(3)–S(2)	125.0(4)	S(3)–C(3)–S(1)	121.2(3)
S(2)–C(3)–S(1)	113.9(3)	C(5)–C(4)–S(5)	117.0(5)
C(4)–C(5)–S(6)	119.6(5)	C(7)–C(6)–S(4)	115.9(5)
C(6)–C(7)–S(6)	113.0(5)		
C(3)–S(1)–C(1)	97.2(3)	C(3)–S(2)–C(2)	97.3(3)
C(3)–S(3)–Ag	107.7(2)	C(1)#2–S(4)–C(6)	99.4(3)
C(1)#2–S(4)–Ag	103.3(2)	C(6)–S(4)–Ag	98.1(2)
C(2)#2–S(5)–C(4)	100.8(3)	C(2)#2–S(5)–Ag	99.2(2)
C(4)–S(5)–Ag	102.1(2)	C(5)–S(6)–C(7)	103.2(3)
C(5)–S(6)–Ag	100.5(2)	C(7)–S(6)–Ag	102.9(2)
S(3)–Ag–S(6)	134.07(6)	S(3)–Ag–S(4)	141.34(5)
S(6)–Ag–S(4)	84.09(5)	S(3)–Ag–S(5)	107.27(5)
S(6)–Ag–S(5)	80.45(5)	S(4)–Ag–S(5)	81.38(5)

the thioether L is preorganised, and is thus eminently suited to facial coordination to appropriate soft metal atoms, as shown by the correspondence between the conformation of the ligand L in the free[8] and bound state. However, in contrast to the well-studied, tridentate thioether **9S3**, L acts as bridging ligand due to the additional thione sulfur. In order to design a neat tridentate ligand, avoiding this complication, we have replaced the thione donor atom of L by oxygen.

Silver(I) Complexes of L′

The silver complexes of the resulting 2,5,8,10,12-pentathiabicyclo[7.3.0]dodeca-1(9)-ene-11-one (L′) are prepared conveniently, in good yields, by reaction of L′ and different silver salts in a 2:1 ratio in acetonitrile. The complexes $[Ag(L')_2]X$ (**5**, **7**–**8**: X = NO_3^-, BF_4^-, PF_6^-) thus formed are colourless solids. The reaction of L′ with silver perchlorate afforded crystals suitable for X-ray diffraction studies. The compound $[Ag(L')_2]ClO_4$ **6** crystallized in the triclinic space group $P\bar{1}$ with two molecules per unit cell (Figure 2). The silver(I) ion is in a pseudo-octahedral environment of six sulfur atoms provided by the two facially coordinating tridentate thioether ligands L′. The Ag–S distances range from 2.709(1) to 2.797(1) Å [Ag–S(6) and Ag–S(8), respectively]; the intraligand S–Ag–S bond angles average 78.5° whereas the corresponding interligand S–Ag–S angles range from 82.49(4)° to 125.15(4)° [S(2)–Ag–S(8) and (S(1)–Ag–S(7), respectively, Table 2]. The comparable thioether complex $[Ag(\mathbf{9S3})_2]^+$ shows similar structural features (Ag–S distances average 2.72 Å; chelating S–Ag–S angles average 80°, non-chelating average 100°)[10,12].

The X-ray structure analysis of the ligand L′ (2,5,8,10,12-pentathia-bicyclo[7.3.0]dodeca-1(9)-ene-11-one), shown in Figure 3, reveals that this tridentate ligand is conformationally well-suited for trigonal, facial coordination. Ligand bond and torsional angles in free L′ (see Table 3) match those of $[Ag(L')_2]ClO_4$ **6** (see Table 2) closely. Thus coordination of L′ to Ag^I necessitates only negligible change in the conformation.

Figure 1. Two views of the molecular structure of $[(AgL)_n](PF_6)_n \cdot 1.5\ n\ CH_3CN$ **4**, H atoms omitted

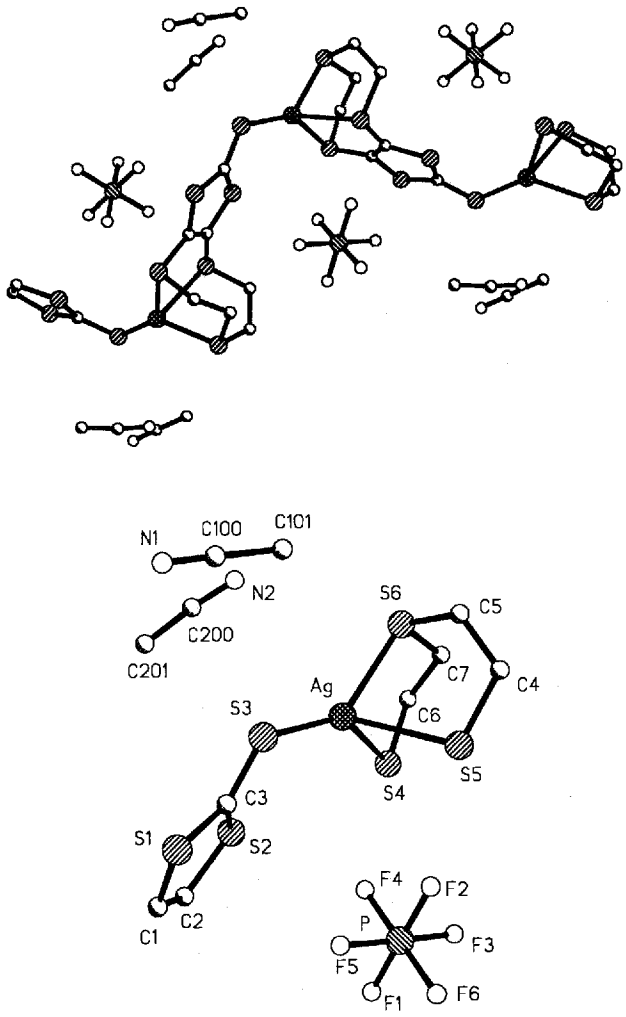


Figure 2. View of the molecular structure of $[Ag(L')_2]ClO_4$ **6**, H atoms omitted

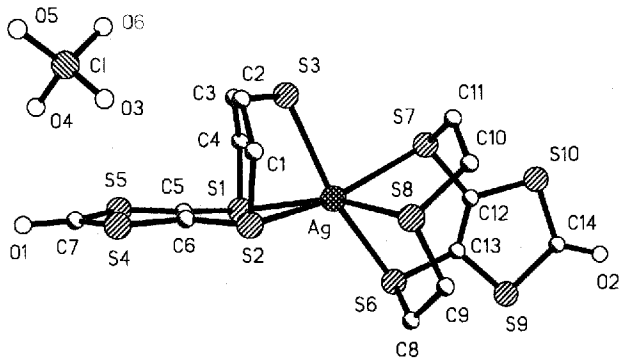
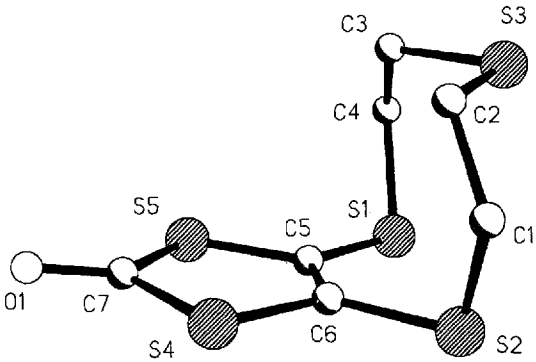


Table 2. Selected bond lengths [Å] and angles [°] for $[Ag(L')_2]ClO_4$ **6**

Ag–S(6)	2.7086(14)	S(4)–C(7)	1.770(6)	S(10)–C(12)	1.746(5)
Ag–S(3)	2.7213(13)	S(4)–C(6)	1.749(5)	S(10)–C(14)	1.768(8)
Ag–S(7)	2.7292(14)	S(5)–C(5)	1.739(5)	O(1)–C(7)	1.201(7)
Ag–S(2)	2.7338(13)	S(5)–C(7)	1.782(6)	O(2)–C(14)	1.204(8)
Ag–S(1)	2.7744(14)	S(6)–C(8)	1.831(6)	C(1)–C(2)	1.520(7)
Ag–S(8)	2.7970(13)	S(6)–C(13)	1.767(6)	C(3)–C(4)	1.500(8)
S(1)–C(5)	1.762(5)	S(7)–C(11)	1.817(6)	C(5)–C(6)	1.343(7)
S(1)–C(4)	1.834(6)	S(7)–C(12)	1.759(5)	C(8)–C(9)	1.512(8)
S(2)–C(6)	1.760(5)	S(8)–C(10)	1.828(5)	C(10)–C(11)	1.509(8)
S(2)–C(1)	1.827(5)	S(8)–C(9)	1.821(6)	C(12)–C(13)	1.350(8)
S(3)–C(3)	1.820(5)	S(9)–C(13)	1.743(5)		
S(3)–C(2)	1.835(5)	S(9)–C(14)	1.779(8)		
S(6)–Ag–S(3)	161.16(5)	C(13)–S(9)–C(14)	96.5(3)
S(6)–Ag–S(7)	76.16(4)	C(12)–S(10)–C(14)	96.3(3)
S(3)–Ag–S(7)	86.84(4)	C(2)–C(1)–S(2)	116.9(4)
S(6)–Ag–S(2)	118.02(4)	C(1)–C(2)–S(3)	116.5(4)
S(3)–Ag–S(2)	80.39(4)	C(4)–C(3)–S(3)	116.5(4)
S(7)–Ag–S(2)	152.65(4)	C(3)–C(4)–S(1)	115.8(4)
S(6)–Ag–S(1)	100.77(4)	C(6)–C(5)–S(5)	117.3(4)
S(3)–Ag–S(1)	78.56(4)	C(6)–C(5)–S(1)	125.2(4)
S(7)–Ag–S(1)	125.15(4)	S(5)–C(5)–S(1)	117.3(3)
S(2)–Ag–S(1)	77.02(4)	C(5)–C(6)–S(2)	127.4(4)
S(6)–Ag–S(8)	79.43(4)	C(5)–C(6)–S(4)	117.1(4)
S(3)–Ag–S(8)	108.65(4)	S(2)–C(6)–S(4)	115.5(3)
S(7)–Ag–S(8)	77.78(4)	O(1)–C(7)–S(4)	124.4(5)
S(2)–Ag–S(8)	82.49(4)	O(1)–C(7)–S(5)	124.0(5)
S(1)–Ag–S(8)	156.86(4)	S(4)–C(7)–S(5)	111.6(3)
C(5)–S(1)–C(4)	100.3(3)	C(9)–C(8)–S(6)	116.2(4)
C(5)–S(1)–Ag	103.8(2)	C(8)–C(9)–S(8)	116.7(4)
C(4)–S(1)–Ag	95.2(2)	C(11)–C(10)–S(8)	116.2(4)
C(6)–S(2)–C(1)	102.2(2)	C(10)–C(11)–S(7)	117.2(4)
C(6)–S(2)–Ag	104.3(2)	C(13)–C(12)–S(7)	125.0(4)
C(1)–S(2)–Ag	93.7(2)	C(13)–C(12)–S(10)	117.7(4)
C(3)–S(3)–C(2)	101.7(2)	S(7)–C(12)–S(10)	117.1(3)
C(3)–S(3)–Ag	104.3(2)	C(12)–C(13)–S(9)	116.9(4)
C(2)–S(3)–Ag	102.2(2)	C(12)–C(13)–S(6)	127.0(4)
C(6)–S(4)–C(7)	97.0(3)	S(9)–C(13)–S(6)	116.1(3)
C(5)–S(5)–C(7)	97.0(2)	O(2)–C(14)–S(9)	123.6(7)
C(13)–S(6)–C(8)	99.9(2)	O(2)–C(14)–S(10)	123.8(7)
C(13)–S(6)–Ag	103.9(2)	S(9)–C(14)–S(10)	112.5(3)
C(8)–S(6)–Ag	96.4(2)	C(12)–S(7)–C(11)	102.1(3)
C(12)–S(7)–Ag	103.9(2)	C(9)–S(8)–C(10)	102.5(3)
C(11)–S(7)–Ag	96.6(2)	C(10)–S(8)–Ag	103.2(2)
C(9)–S(8)–Ag	101.8(2)		

Figure 3. View of the molecular structure of 2,5,8,10,12-pentathiabicyclo[7.3.0]dodeca-1(9)-ene-11-one **L'**, H atoms omitted



The conformational and metal-binding properties of the silver complexes **5**, **7**, and **8** $[Ag(L')_2]X$ ($X = NO_3^-$, BF_4^-, PF_6^-) should be similar, as indicated by their spectroscopic and elemental analysis data.

These results underscore the resemblance of the small thioether ligands investigated here to their saturated analogue 1,4,7-trithiacyclononane (**9S3**)[10–12].

Table 3. Bond lengths [Å] and angles [°] for 2,5,8,10,12-pentathiabicyclo[7.3.0]dodeca-1(9)-ene-11-one (**L'**)

S(1)–C(5)	1.747(3)	S(1)–C(4)	1.824(3)
S(2)–C(6)	1.757(3)	S(2)–C(1)	1.835(3)
S(3)–C(2)	1.809(3)	S(3)–C(3)	1.822(3)
S(4)–C(6)	1.748(3)	S(4)–C(7)	1.773(4)
S(5)–C(5)	1.756(3)	S(5)–C(7)	1.767(4)
O(1)–C(7)	1.205(4)	C(1)–C(2)	1.526(4)
C(3)–C(4)	1.516(4)	C(5)–C(6)	1.347(4)
C(5)–S(1)–C(4)	100.02(12)	C(6)–S(2)–C(1)	100.50(13)
C(2)–S(3)–C(3)	102.84(14)	C(6)–S(4)–C(7)	97.0(2)
C(5)–S(5)–C(7)	96.9(2)	C(2)–C(1)–S(2)	115.6(2)
C(1)–C(2)–S(3)	115.9(2)	C(4)–C(3)–S(3)	115.8(2)
C(3)–C(4)–S(1)	116.2(2)	C(6)–C(5)–S(1)	124.7(3)
C(6)–C(5)–S(5)	117.0(3)	S(1)–C(5)–S(5)	118.4(2)
C(5)–C(6)–S(4)	117.0(3)	C(5)–C(6)–S(2)	124.7(3)
S(4)–C(6)–S(2)	118.3(2)	O(1)–C(7)–S(5)	123.9(4)
O(1)–C(7)–S(4)	124.1(4)	S(5)–C(7)–S(4)	112.0(2)

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Experimental Section

The ligands L and L' were prepared according to literature procedures[7]. The silver salts were purchased from Aldrich. – Melting points: Hot-stage microscope (Boëtius), uncorrected values. – IR: Perkin-Elmer 1725, KBr pellets (200–4000 cm^{-1}). – ^1H NMR: Varian Unity 400 (400.13 MHz), [D$_6$]DMSO-containing 1% tetramethylsilane ($\delta_H = 0$). – ^{13}C NMR: Varian Unity 400 (100.61 MHz), [D$_6$]DMSO-containing 1% tetramethylsilane ($\delta_C = 0$). – MS: ZAB-HSQ (VG Analytical). – Elemental analysis: Heraeus CHN Rapid Analyser.

Synthesis of the Silver Complexes $[AgL]_nX_n$ ($X = NO_3^-$, ClO_4^-, BF_4^-, PF_6^-) **1**–**4**: 47.7 mg (0.17 mmol) 2,5,8,10,12-Pentathiabicyclo[7.3.0]dodeca-1(9)-ene-11-thione (L) was dissolved in acetonitrile (30 ml) at 60 °C, and the corresponding silver salt (0.17 mmol), dissolved in acetonitrile (5 ml), was added with stirring. Following the addition, the mixture was cooled to room temp. The solvent was removed, yielding a yellow solid, which was recrystallized from acetonitrile/2-propanol.

(2,5,8,10,12-Pentathiabicyclo[7.3.0]dodeca-1(9)-ene-11-thione)silver(I) Nitrate $\{[(AgL)_n](NO_3)_n$, **1**$\}$: Yield 52 mg (69%), m.p. 160 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2950 and 2910 cm^{-1} (CH), 1415, 1385, 1330 and 1280 (NO_3), 1025 (C=S). – ^1H NMR: δ = 3.28 (t, ^3J = 6 Hz, 4H, $-CH_2-S-C=$), 3.06 (t, ^3J = 6 Hz, 4H, $-CH_2-S$). – ^{13}C NMR: δ = 212.0 (C=S), 140.0 (C=C), 36.2 and 33.3 ($-CH_2-S$). – MS (FAB) *m/z* (%) = 392 (17) $[AgL]^+$. – $(C_7H_8AgNO_3S_6)_n$ (454.4)$_n$: calcd. C 18.50, H 1.77, N 3.08, S 42.34; found C 18.46, H 1.99, N 3.07, S 42.33.

(2,5,8,10,12-Pentathiabicyclo[7.3.0]dodeca-1(9)-ene-11-thione)silver(I) Perchlorate $\{[(AgL)_n](ClO_4)_n$, **2**$\}$: Yield 70 mg (83%), m.p. 145 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2960 and 2900 cm^{-1} (CH), 1085 and 625 (ClO_4), 1025 (C=S). – ^1H NMR: δ = 3.30 8t, ^3J = 6 Hz, 4H, $-CH_2-S-C=$), 3.05 (t, ^3J = 6 Hz, 4H, $-CH_2-S$). – ^{13}C NMR: δ = 212.0 (C=S), 140.0 (C=C), 36.3 and 32.4 ($-CH_2S$). – $(C_7H_8AgClO_4S_6)_n$ (553.9)$_n$: calcd. C 17.10, H 1.64, O 13.01, S 39.11; found C 17.30, H 1.87, O 14.00, S 39.91.

(2,5,8,10,12-Pentathia-bicyclo[7.3.0]dodeca-1(9)-ene-11-thione)silver(I) Tetrafluoroborate $\{[(AgL)_n](BF_4)_n$, **3**$\}$: Yield 66 mg (83%), m.p. 153 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2980 and 2930 cm^{-1} (CH), 1120, 1075, 1050 and 1020 (BF_4 and C=S). – ^1H NMR: δ = 3.31 (t, ^3J = 6 Hz, 4H, $-CH_2-S-C=$), 3.04 (t, ^3J = 6 Hz, 4H, $-CH_2-S$). – ^{13}C NMR: δ = 212.0 (C=S), 140.0 (C=C), 36.3

and 32.7 ($-CH_2-S$). – MS (FAB) *m/z* (%) = 392 (12) $[AgL]^+$. – $(C_7H_8AgBF_4S_6)_n$ (479.2)$_n$: calcd. C 17.55, H 1.68, S 40.14; found C 18.10, H 1.87, S 38.05.

(2,5,8,10,12-Pentathiabicyclo[7.3.0]dodeca-1(9)-ene-11-thione)-silver(I) Hexafluorophosphate {$[(AgL)_n](PF_6)_n$, **4**}: Yield 76 mg (85%), m.p. 200°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1050 cm^{-1} (C=S), 835 and 560 (PF_6). – ^1H NMR: δ = 3.32 (t, ^3J = 6 Hz, 4H, $-CH_2-S-C=$), 3.05 (t, ^3J = 6 Hz, 4H, $-CH_2-S$). – ^{13}C NMR: δ = 212.1 (C=S), 140.1 (C=C), 36.2 and 32.1 ($-CH_2-S$). – $(C_7H_8AgF_6PS_6)_n$ (537.4)$_n$: calcd. C 15.65, H 1.50, N 0.0, P 5.76, S 35.80; found C 16.11, H 1.59, N 0.2, P 5.78, S 34.58.

Table 4. Crystal and refinement data for $[(AgL)_n](PF_6)_n \cdot 1.5\ n\ CH_3CN$ (**4**), $[Ag(L')_2]ClO_4$ (**6**), and $C_7H_8OS_5$ (**L'**)

	4	**6**	**L'**
Formula	$C_{10}H_8AgF_6N_{1.5}PS_6$	$C_{14}H_{16}AgClO_6S_{10}$	$C_7H_8OS_5$
Formula weight	594.38	744.19	268.43
Temperature [K]	173(2)	243(2)	293(2)
Wavelength [Å]	0.71069	0.71069	0.71069
Measurement device	CAD4-MACH3	CCD SMART(Fa. Siemens)	
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/a$	$P\bar{1}$	$P2_1/c$
a [Å]	12.642(1)	8.7076(6)	11.548(2)
b [Å]	14.201(1)	11.0806(8)	6.4400(10)
c [Å]	12.661(1)	12.9452(9)	14.680(3)
α [°]	90	92.642(1)	90
β [°]	117.60(1)	97.494(1)	90.11(3)
γ [°]	90	97.331(1)	90
V [Å^3]	2014.3(3)	1225.7(2)	1091.7(3)
Z	4	2	4
d_c [g cm^{-3}]	1.960	2.016	1.663
μ [mm^{-1}]	1.752	1.815	1.018
F(000)	1162	744	552
Crystal appearance	yellow prism	colourless plate	colourless needle
Crystal size [mm^3]	0.5 × 0.3 × 0.3	0.42 × 0.38 × 0.28	1.10 × 0.60 × 0.23
θ range collection [°]	1.81 to 25.01	1.59 to 25.90	1.39 to 26.41
Index ranges	$0 \le h \le 15$	$-7 \le h \le 10$	$-14 \le h \le 11$
	$-16 \le k \le 0$	$-13 \le k \le 10$	$-8 \le k \le 7$
	$-15 \le l \le 13$	$-13 \le l \le 15$	$-18 \le l \le 18$
Refl. collected	3714	5438	4785
Refl independent	3537	4096	2080
R_{int}	0.0356	0.0577	0.0413
Refinement method	full-matrix least-squares on F^2		
Data / restraints / parameters	3537 / 0 / 214	4096 / 21 / 341	2080 / 0 / 140
GoF	1.056	1.099	1.111
*R*1 [2σ(I)]	0.0511	0.0435	0.0341
*wR*2 [2σ(I)]	0.1234	0.1429	0.0917
*R*1 (all data)	0.0649	0.0503	0.0388
*wR*2 (all data)	0.1311	0.1519	0.0997
Largest diff. peak and hole [eÅ^{-3}]	1.318 and –1.153	0.936 and –0.836	0.288 and –0.317

Synthesis of the Silver Complexes $[AgL'_2]X$ ($X = NO_3^-$, ClO_4^-, BF_4^-, PF_6^-) **5**–**8**: 37.5 mg (0.14 mmol) 2,5,8,10,12-Pentathia-bicyclo[7.3.0]dodeca-1(9)-ene-11-one (L') was dissolved in acetonitrile (30 ml) at 60°C, and the corresponding silver salt (0.07 mmol), dissolved in acetonitrile (5 ml), was added with stirring. Following the addition, the mixture was cooled to room temperature. The solvent was removed, yielding a white solid, which was washed with chloroform and methanol.

Bis(2,5,8,10,12-pentathiabicyclo[7.3.0]dodeca-1(9)-ene-11-one)silver(I) Nitrate {$[Ag(L')_2]NO_3$, **5**}: Yield 37 mg (75%), m.p. 182°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2952 and 2920 cm^{-1} (CH), 1663 and 1608 (C=O), 1412, 1385, 1339, 1317, 1304 and 1278 (NO_3). – ^1H NMR: δ = 3.23 (t, ^3J = 6 Hz, 4H, $-CH_2-S-C=$), 3.07 (t, ^3J = 6 Hz, 4H, $-CH_2-S$). – ^{13}C NMR: δ = 189.1 (C=O), 130.4 (C=C), 36.6 and 33.9 ($-CH_2-S$). – $C_{14}H_{16}AgNO_5S_{10}$ (706.8): calcd. C 23.79, H 2.28, N 1.98, S 45.37; found C 24.12, H 2.27, N 1.96, S 46.24.

Bis(2,5,8,10,12-pentathia-bicyclo[7.3.0]dodeca-1(9)-ene-11-one)silver(I) Perchlorate {$[Ag(L')_2]ClO_4$, **6**}: Yield 52 mg (85%), m.p. 232°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2915 cm^{-1} (CH), 1669 (C=O), 1084 and 625 cm^{-1} (ClO_4). – ^1H NMR: δ = 3.27 (t, ^3J = 6 Hz, 4H, $-CH_2-S-C=$), 3.04 (t, ^3J = 6 Hz, 4H, $-CH_2-S$). – ^{13}C NMR: δ = 188.5 (C=O), 130.0 (C=C), 36.4 and 33.4 ($-CH_2-S$). – $C_{14}H_{16}AgClO_6S_{10}$ (744.2): calcd. C 22.59, H 2.17, S 43.08, Cl 4.76; found C 22.75, H 2.12, S 42.29, Cl 3.74.

Bis(2,5,8,10,12-pentathiabicyclo[7.3.0]dodeca-1(9)-ene-11-one)silver(I) Tetrafluoroborate {$[Ag(L')_2]BF_4$, **7**}: Yield 30 mg (59%), m.p. 258°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2947 and 2919 cm^{-1} (CH), 1670 and 1607 (C=O), 1084, 1056 and 1028 (BF_4). – ^1H NMR: δ = 3.25 (t, ^3J = 6 Hz, 4H, $-CH_2-S-C=$), 3.03 (t, ^3J = 6 Hz, 4H, $-CH_2-S$). – ^{13}C NMR: δ = 188.7 (C=O), 130.0 (C=C), 36.3 and 33.7 ($-CH_2-S$). – $C_{14}H_{16}AgBF_4O_2S_{10}$ (731.6): calcd. C 22.98, H 2.20, S 43.83; found C 23.22, H 2.21, S 44.07.

Bis(2,5,8,10,12-pentathia-bicyclo[7.3.0]dodeca-1(9)-ene-11-one)silver(I) Hexafluorophosphate {$[Ag(L')_2]PF_6 \cdot 0.33\ CH_3CN$, **8**}: Yield 34 mg (62%), m.p. 218°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2951 and 2919 cm^{-1} (CH), 1671 and 1608 (C=O), 837 and 558 (PF_6). – ^1H NMR: δ = 3.27 (t, ^3J = 6 Hz, 4H, $-CH_2-S-C=$), 3.05 (t, ^3J = 6 Hz, 4H, $-CH_2-S$). – ^{13}C NMR: δ = 188.4 (C=O), 129.9 (C=C), 36.2 and 33.2 ($-CH_2-S$). $C_{14}H_{16}AgPF_6O_2S_{10} \cdot 0.33\ CH_3CN$ (803.3): calcd. C 21.92, H 2.13, N 0.58, S 39.92; found C 22.13, H 2.33, N 0.6, S 36.92.

Crystal Structure Analyses of $[(AgL)_n](PF_6)_n \cdot 1.5\ n\ CH_3CN$ **4**, *$[Ag(L')_2]ClO_4$* **6**, *and 2,5,8,10,12-Pentathia-bicyclo[7.3.0]dodeca-1(9)-ene-11-one (L')*: Crystal data and crystallographic experimental data are listed in Table 4.

A well-shaped crystal of **4** was mounted in a cold nitrogen stream owing to decay by solvent loss. In order to obtain a smaller standard deviation of the atomic coordinates, **6** was also measured in a cold nitrogen stream (243 K). The structures of **4** and **L'** were solved by direct methods (SHELXS-86)[13], while the solution of the structure of **6** was carried out by heavy-atom procedures (SHELXS-86)[13]. The structures were refined by full-matrix least-squares techniques against F^2 (SHELXL-93)[14]. SHELXTPLUS[15] was used for structure representations. Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-405937 (**4**), CSD-405954 (**6**) or CSD-495955 (**L'**), the names of the authors, and the journal citation.

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