Dimeric Silver(I) Complexes of Some Isothiazole-Based Ligands☆

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A series of isothiazole-based potential ligands bearing substituents with additional donor sites in the 5-position of the heterocycle was synthesized [3-Me-5-R-C_3HNS; R = $CH{=}N(CH_2)_2py$ (**1**), $CH{=}NCH_2py$ (**2**), $CH_2N(CH_2CH_2NEt_2)_2$ (**4**), $(CH_2)_2SMe$ (**5**)]. Upon reaction with AgO_3SCF_3 they formed complexes $[(\mathbf{1})AgOSO_2CF_3]_2$ (**6**), $[(\mathbf{2})AgOSO_2CF_3]_2$ (**7**), $[(\mathbf{4})Ag]_2^{2+}(O_3SCF_3^-)_2$ (**8**) and $[(\mathbf{5})AgOSO_2CF_3]_2$ (**9**), respectively. **6**, **8** and **9** were shown by X-ray structural analyses to consist of dimeric units $L_2Ag_2^{2+}$, either discrete (**8**), coordinated by terminal $CF_3SO_3^-$ ligands (**9**) or linked via bridging $CF_3SO_3^-$ units (**6**). In **8** and **9** the isothiazole moiety is bonded to the metal center via the ring-N. The coordination potential of the isothiazole heterocycle is discussed.

Introduction

The study of molecular self assembly in coordination chemistry, i.e. the formation of di- and oligonuclear aggregates from metals and specific polydentate ligands, is a rapidly growing area[1]. Due to the relevance of self assembly in nature the investigation of ligands having mixed N/S donor sites receives particular attention. We report on the formation of dinuclear Ag complexes of a series of isothiazole-based ligands providing both nitrogen and sulfur as potential donor atoms in the heterocycle.

A further motivation for this study arises from the interest in dinuclear complexes showing cooperative phenomena, especially for the activation of small substrate molecules[2]. The ability of symmetric diazine heterocycles, e.g. pyrazoles, to fix two metal centers at a favourable distance of 3.4 to 4.6 Å is well documented[3]. In order to introduce unsymmetric ligand sets based on this structural motif, i.e. different coordination spheres for the two metals, one might (a) attach different chelating side arms at the diazine nucleus or (b) incorporate different donor atoms within the heterocyclic bridge. With the latter approach in mind, the present work aims at elucidating the coordination potential of the ring sulfur in isothiazole-based molecules.

Only few reports on the coordination chemistry of isothiazoles have appeared in the literature[4–7] and to our knowledge only one complex has been characterized crystallographically by X-ray diffraction, namely $[en_2Co(C_3H_2NSCO_2)]^{2+}$ (**I**) (en = ethylenediamine)[7]. It shows a 3-carboxyisothiazole bonded to a cobalt(III) moiety through the ring nitrogen atom and the exocyclic carboxylate functionality. Likewise a coordination of the nitrogen atom is proposed in most of the other complexes of transition-metal ions with simple isothiazoles[4]. Only in two cases a bonding of the ring sulfur atom to Hg^{II}[5] or to a $Mo(CO)_5$ fragment[6] is suggested on the basis of IR and NMR evidence. Considering the weak tendency of thiophene to bind as a sulfur-donor ligand towards transition metals[8] it was expected to be difficult to achieve η^1-*S* coordination in isothiazole complexes. Moreover, the electron density at the sulfur atom should be even lower in the case of isothiazole compared to thiophene according to ab initio calculations[9]. Hence this study deals with isothiazole compounds bearing substituents with additional chelating donor sites in 5-position of the heterocycle in order to possibly support coordination of the ring sulfur atom. As sulfur donors are known to be good ligands for group-11 cations, particularly in their low oxidation state, complexes with silver(I) were examined.

$[en_2Co(C_3H_2NSCO_2)]^{2+}$ **I** (en: ethylenediamine)

Preparation of Compounds

Simple isothiazoles were functionalized in order to obtain the desired ligands. 5-Formyl-3-methylisothiazole[10] and 3,5-dimethylisothiazole[11] are accessible via several steps from purchasable starting materials according to known procedures and can be further modified (Scheme 1). Reaction of the former with the appropriate primary amines yields the imines **1** and **2**, each having two potential nitrogen donors in the substituent. Bromination of 3,5-dimethylisothiazole and subsequent treatment of the resulting bromomethylisothiazole **3** with *N*,*N*,*N*′,*N*′-tetraethyldiethylenetriamine in the presence of triethylamine affords the multidentate compound **4**. Alternatively, 3,5-dimethylisothiazole can be lithiated by means of LDA[12] and then alkylated with chloromethyl methyl sulfide to yield **5**, which provides a single thioether donor site in the side arm.

For the syntheses of silver(I) complexes, the solutions of functionalized isothiazoles **1**, **2**, **4** or **5** in Et_2O were added to a solution of silver trifluoromethanesulfonate in Et_2O

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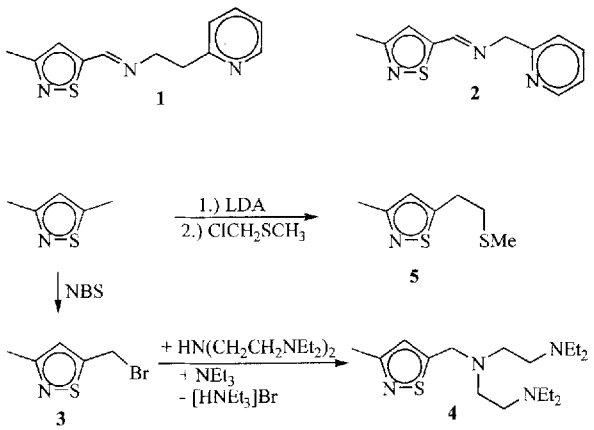
Scheme 1



under exclusion of light, causing the immediate precipitation of complexes **6**, **7**, **8** and **9** as white or yellowish solids. These were filtered off and dried in vacuo to afford the products in analytically pure state. The complexes **6**, **8** and **9** are moderately light- and air-sensitive compounds, while **7** is stable on exposure to light for prolonged periods (hours). **7** and **8** show good solubilities in acetone and dichloromethane. In contrast, **6** and **9** are only soluble in very polar solvent such as DMSO or DMF.

$[LAgOSO_2CF_3]_2$ $[LAg]_2^{2+}(O_3SCF_3^-)_2$

6: L = **1** **8**: L = **4**
7: L = **2**
9: L = **5**

The formation of coordination complexes is corroborated by the FAB-MS spectra, which show species LAg^+ (L = **1**, **2**, **4**, **5**) with the expected isotopic distribution as most intense peaks in all cases. However, fragments with higher masses can be detected as well, e.g. peaks corresponding to $L_2Ag_2(O_3SCF_3)^+$ (L = **1**, **2**), $LAg_2[N(CH_2CH_2NEt_2)_2](O_3SCF_3)^+$ (L = **4**) and $L_2Ag_2(O_3SCF_3)^+$ (L = **5**). This suggests the presence of complexes of higher nuclearity as confirmed by X-ray structural determinations for **6**, **8** and **9** (see below). IR spectra of all complexes (**6**–**9**) predominantly show bands characteristic for triflate anions. Thus, the typical resonances of the isothiazole ring system[13] which could give some information on whether the heterocycle is involved in the coordination of the silver ions [ν(C=C) at $\tilde{\nu} \approx 1530$ cm^{-1}; ν(C=N) at $\tilde{\nu} \approx 1400$ cm^{-1}; ν(S–N) at $\tilde{\nu} \approx 810$ cm^{-1}] can not be assigned unambiguously. The $\nu(C{=}N)_{imine}$ frequencies at $\tilde{\nu} \approx 1635$ cm^{-1} in **1**, **2** and **6**, **7** do not show significant changes upon coordination. The bands in the triflate stretching region ($\tilde{\nu}$ = 1400–1000 cm^{-1})[14] of **6**–**9** are similar, hence not allowing a definite identification of different binding modes of the counteranion. In order to elucidate the coordination modes in **6**–**9**, X-ray crystallographic determinations were carried out except in the case of **7**, for which no suitable crystals could be obtained.

Solid-State Structures

6 crystallizes in space group $P\bar{1}$. The structure determination reveals the presence of dimeric species $L_2Ag_2^{2+}$ (Figure 1) being linked by bridging triflate anions as depicted in Figure 2. Inspection of the dinuclear unit shows that the metal centers are each bonded to the imine-N of one ligand [Ag1–N2A 2.199(2) Å] and the pyridine-N of a second ligand [Ag1–N1 2.226(2) Å]. Due to the additional coordination of two triflate ions via long Ag–O bonds [2.605(2) Å and 2.568(2) Å] the angle N1–Ag1–N2A [153.95(8)°] deviates considerably from linearity. The four N atoms (imine and pyridine) of the dimeric unit lie within a plane with the two silver ions situated 50 pm above and below this plane. The distance between the two metal centers amounts to 4.6 Å. The isothiazole ring systems and the respective CH=N moieties are nearly coplanar (torsion angle S1–C9–C8–N2 8.9°) with the isothiazole-imine skeleton adopting the favorable *s-cis* conformation. While leaving the conjugation between the isothiazole and the imine π system intact, this causes the sulfur atom to lie in the proximity of the silver cation. However, the Ag–S distance (3.047 Å) still is slightly longer than the maximum bond distance generally accepted for Ag^I–S bonds (3.01 Å)[15] and indicates at best very weak interactions. Similar Ag–S distances had been observed by van Koten et al. in a series of related thiophene-imine complexes with Ag^I[15,16]. Detailed NMR-spectroscopic investigations suggested in those cases the S(thiophene)–Ag interaction to be of negligible bonding character and to consist of no more than a dipole-cation attraction[15]. As a consequence of the *s-cis* conformation of the coplanar isothiazole-imine skeleton we assume this to also prove true for the present complex **6**. Further conclusions in this regard should be deducible from the structures of complexes **8** and **9** having more flexible side arms without a double bond. Furthermore the differing number of donor sites in the substituents of **1**, **4** and **5** might influence the extent of aggregation in the resulting coordination compounds.

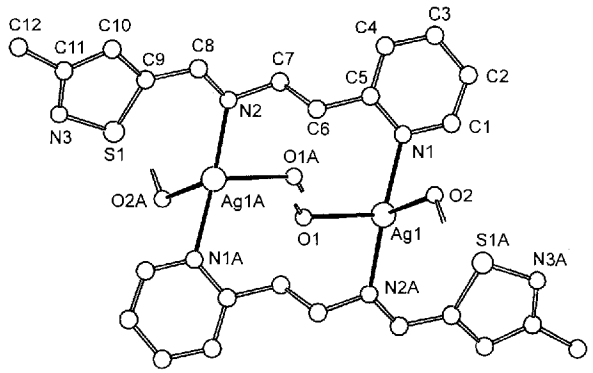
Complex **8** crystallizes in the monoclinic space group $P2_1/c$. It consists of a cyclic dimer built from two silver ions and two molecules of **4** as depicted in Figure 3.

The O_3SCF_3 anions are non-coordinating. Each silver ion is bonded to four nitrogen donors, i.e. three from the side arm of one ligand molecule and the ring-N of a second ligand molecule. The latter forms the shortest bond [*d*(Ag1–N1A) 2.297(4) Å] due to its sp^2 character. Because of the steric strain in the bis[(diethylamino)ethyl]amino framework of the ligand side arm, the coordination geometry around the silver ion is considerably distorted from tetrahedral. The shortest Ag–S distance amounts to 3.39 Å which clearly rules out any bonding interaction.

Compound **9** crystallizes in space group $P\bar{1}$. As in the case of **8**, a cyclic array of two silver ions and two molecules of **5** is formed, as shown in Figure 4.

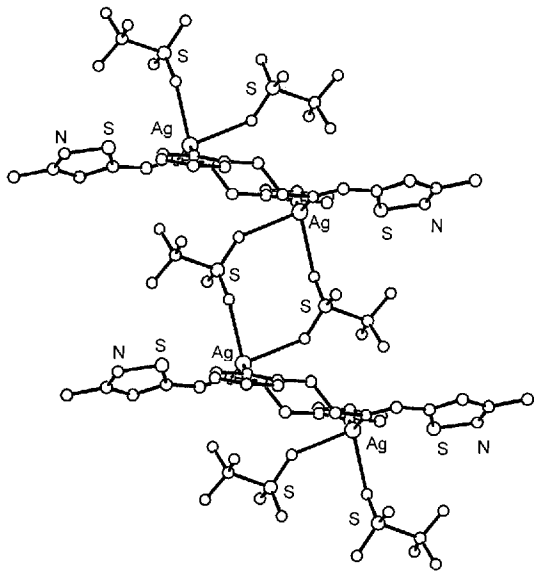
The coordination sphere around each silver ion is trigonal planar and consists of an isothiazole-N, a sulfur atom from the side arm of a second molecule of **5** and an *O*-

Figure 1. The dimeric unit of **6**; in the interests of clarity only the coordinating oxygen atoms of the triflates are shown and all hydrogen atoms have been omitted[a]



[a] Selected distances [Å] and angles [°]: Ag1–N1 2.226(2), Ag1–N2A 2.199(2), Ag1–S1A 3.047, Ag1–O1 2.605(2), Ag1–O2 2.568(2), N2–C8 1.276(3), C8–C9 1.451(4), C9–S1 1.708(3), S1–N3 1.659(3), N3–C11 1.307(4); N1–Ag1–N2A 153.95(8), N2A–Ag1–O2 119.93(7), N1–Ag1–O2 80.77(7), O1–Ag1–O2 88.40, S1–C9–C8–N2 8.93.

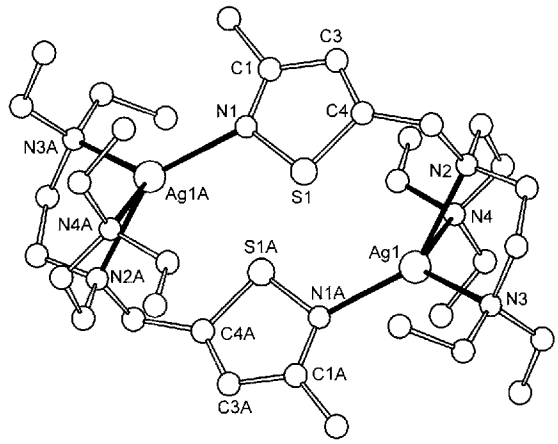
Figure 2. Linking of the dimeric units $L_2Ag_2^{2+}$ (L = **1**) in **6** by bridging triflates; for the sake of clarity all hydrogen atoms have been omitted



bonded O_3SCF_3 counterion. The bond lengths Ag1–S3 [2.437(2) Å] and Ag2–S4 [2.421(1) Å] lie within the range expected from literature values for Ag^I–S(thioether) bonds, i.e. 2.40–2.70 Å[17]. The shortest Ag–S(isothiazole) distance in **9** is 3.49 Å, thus ruling out any bonding interaction in agreement with the findings for **8** mentioned above.

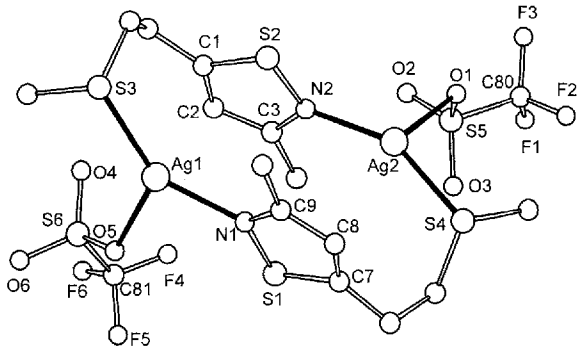
Comparison of the geometry of the isothiazole ring skeletons in **6**, **8** and **9** reveals no significant changes upon N-coordination of the heterocycle. The N–S distances in **8** [1.671(4) Å] and **9** [1.672(4)/1.674(3) Å] are similar to that found for the only other structurally characterized isothiazole complex **I** mentioned above [1.666(5) Å][7] and are only slightly longer than in the uncoordinated heterocycle in **6** [1.659(3) Å]. The same is true for the adjacent N–C bond,

Figure 3. Molecular structure of the dimeric unit of **8**; the triflate counterions are not shown and in the interests of clarity all hydrogen atoms have been omitted[a]



[a] Selected bond lengths [Å] and angles [°]: Ag1–N1A 2.297(4), Ag1–N2 2.469(4), Ag1–N3 2.387(4), Ag1–N4 2.469(4), N1–C1 1.324(6), N1–S1 1.671(4), S1–C4 1.713(4); N1A–Ag1–N2 145.24(12), N1A–Ag1–N3 125.16(13), N1A–Ag1–N4 107.25(13), N2–Ag1–N3 76.91(12), N2–Ag1–N4 75.85(12), N3–Ag1–N4 119.51(12).

Figure 4. Molecular structure of the dimeric unit of **9**; for the sake of clarity all hydrogen atoms have been omitted[a]



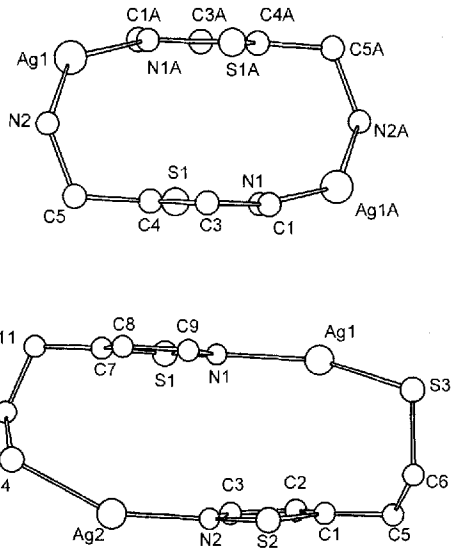
[a] Selected bond lengths [Å] and angles [°]: Ag1–N1 2.213(3), Ag1–S3 2.437(3), Ag1–O5 2.392(4), Ag2–N2 2.169(3), Ag2–S4 2.421(1), Ag2–O1 2.570(3), N1–S1 1.674(4), N1–C9 1.327(5), N2–S2 1.674(3), N2–C3 1.327(6); N1–Ag1–S3 142.36(10), N1–Ag1–O5 95.76(14), S3–Ag1–O5 121.80(11), N2–Ag2–S4 152.55(10), N2–Ag2–O1 100.33(12), S4–Ag2–O1 100.31(9).

which is slightly elongated upon N-coordination to the metal center [**6**: 1.307(4) Å; **8**: 1.324(6) Å; **9**: 1.327(5)/1.327(6) Å; **I**: 1.335(8) Å[7]].

The two isothiazole ring systems of each dimeric unit in both **8** and **9** are approximately coplanar, though not stacked one above another. A view parallel to these planes reveals the presence of cavities spanned by the bimetallic framework (Figure 5).

The distance between the planes of the isothiazole moieties amounts to 3.0 Å (**8**) and 3.3 Å (**9**), respectively, and thus lies in the range found for numerous planar aromatic systems in the solid state[18]. The distance between the laterally limiting atoms of the cavity is 8.69 Å in **8** (N2–N2A) and 9.10 Å in **9** (C6–C12). The two silver ions are 5.83 Å (**8**) and 5.52 Å (**9**) apart from each other. Considering the

Figure 5. View parallel to the isothiazole planes of the dimeric units in **8** (top) and **9** (bottom)



size of the cavities displayed by known host-guest systems, e.g. cyclophane macrocycles, of at least 8 × 8 Å[19] it is unlikely that **8** or **9** might accommodate guest molecules.

Complexes in Solution

NMR spectra of compounds **6**–**9** were recorded as [D_6]acetone solutions (**7**, **8**) and [D_6]DMSO solutions (**6**, **9**). The ^{19}F-NMR spectra of all complexes show one singlet with chemical shifts in the range $\delta = -78.3$ to -77.0 that is characteristic for free uncoordinating O_3SCF_3 anions (solutions of AgO_3SCF_3 in [D_6]acetone and [D_6]DMSO display resonances at $\delta = -78.0$ and -76.7, respectively). Obviously the triflates that were found to *O*-coordinate in the solid-state structures of **6** and **9** are detached from the silver ions upon dissolution in highly polar DMSO. The room-temperature ^{1}H-NMR spectra of complexes **6**–**9** exhibit downfield shifts for most resonances compared to those of the free compounds **1**–**5**. These changes are most notable for the imine-H singlet of **6** and **7** and the isothiazole H^4 singlet in all cases. The latter finding might indicate that in solution the ring-N is involved in coordination of the silver ions not only for **8** and **9**, but also for the isothiazolyl-imine complexes **6** and **7**. It should be noted that the dinuclear cationic units found in the solid state most likely break down or are at least in equilibrium with mononuclear species upon dissolution in coordinating solvents like DMSO, however investigations in other media are hampered by the insolubility of these compounds in nonpolar solvents.

Conclusions

The isothiazole-based compounds **1**, **2**, **4** and **5** bearing substituents with differing topology and differing number of additional donor sites adjacent to the ring-S atom all form dimeric complexes with AgO_3SCF_3, namely [(**1**)AgO$SO_2CF_3]_2$ (**6**), [(**2**)Ag$OSO_2CF_3]_2$ (**7**), $[(\mathbf{4})Ag]_2^{2+}(O_3SCF_3^-)_2$ (**8**) and [(**5**)Ag$OSO_2CF_3]_2$ (**9**). The basic structural motif of dinuclear units $Ag_2L_2^{2+}$ resulting from N-coordination of the isothiazole heterocycles is the same in both **8** and **9**. As a result of the fewer donor sites in the side arm of **5** compared to **4**, the coordinative saturation of the silver ions in **9** is realized by coordination of the O_3SCF_3 counterions. The ring-S atom is not involved in bonding interactions with the metal center in any of the complexes studied; even the only weakly coordinating triflate anion is clearly a better donor towards Ag^1. For complex **6** a formation of dimeric units involving the ring-N as in **8** and **9** is excluded due to steric constraints imposed by the preferentially coplanar isothiazole-imine skeleton. Hence the dinuclear moiety $Ag_2L_2^{2+}$ in **6** is solely set up by coordination of the side arm donor sites while the ring-N atoms remain uncoordinated. The weak coordination potential of the ring-S atom renders isothiazoles unsuitable for the construction of unsymmetric dinuclear complexes based on bridging heterocycles as outlined in the introduction. In this regard it appears more promising to attach different chelating side arms at a diazine bridge, e.g. pyrazolate.

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Experimental Section

All manipulations were carried out under dry nitrogen by employing standard Schlenk techniques. Solvents were dried according to established procedures. Starting compounds were prepared following the literature methods cited. Microanalyses: Analytische Laboratorien Heidelberg. – IR: Bruker IFS 66 FTIR. – ^{1}H and ^{13}C{^{1}H} NMR: Bruker AC 200 at 200.13 MHz and 50.32 MHz, respectively. Signal of the solvent as chemical shift reference. $CDCl_3$: $\delta_H = 7.27$, $\delta_C = 77.0$; [D_6]DMSO: $\delta_H = 2.50$, $\delta_C = 39.5$; [D_6]acetone: $\delta_H = 2.04$, $\delta_C = 29.8$. – ^{19}F NMR: Jeol FX 90 Q at 84.25 MHz, external standard $CFCl_3$. – MS (FAB and EI): Finnigan MAT 8230. – Melting points: Gallenkamp MFB 595010.

3-Methyl-N-[2-(2-pyridyl)ethyl]isothiazol-5-carbaldimine (**1**): A solution of 1.0 g (8.0 mmol) of 5-formyl-3-methylisothiazole[10] and 0.98 g (8.0 mmol) of 2-(2-aminoethyl)pyridine in 50 ml of ethanol was heated to reflux for 3 h. After evaporation of the solvent, 1.7 g (92%) of the product remained in analytically pure form as yellowish oil. – IR (film): $\tilde{\nu} = 1636$ cm^{-1} (C=N), 1534 (C=C), 811 (S–N). – ^{1}H NMR ($CDCl_3$): $\delta = 2.49$ (s, 3H, CH_3), 3.18 (t, $J = 7.6$ Hz, 2H, CH_2), 4.02 (t, $J = 7.6$ Hz, 2H, NCH_2), 7.07–7.27 (m, 3H, aromatic H), 7.57 (m, 1H, aromatic H), 8.28 (s, 1H, CH=N), 8.54 (d, $J = 5.1$ Hz, 1H, aromatic H). – ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 18.7$ (CH_3), 38.8 (CH_2), 60.8 (NCH_2), 121.1 (py-C^3), 123.5 (py-C^5), 124.6 (isothiazole-C^4), 136.0 (py-C^4), 149.1 (py-C^6), 151.9 (CH=N), 158.9 (py-C^2), 163.7, 167.0 (isothiazole-$C^{3/5}$). – MS (70 eV); *m/z* (%): 231 (21) [M^+], 106 (100) [$CH_2CH_2py^+$]. – $C_{12}H_{13}N_3S$ (231.3): calcd. C 62.31, H 5.66, N 18.17; found C 62.09, H 5.77, N 17.89.

3-Methyl-N-[(2-pyridyl)methyl]isothiazol-5-carbaldimine (**2**): Starting from 0.8 g (6.3 mmol) of 5-formyl-3-methylisothiazole[10] and 0.7 g (6.3 mmol) of 2-(aminomethyl)pyridine the preparation was carried out in close analogy to that for **1** to yield 1.2 g (88%) of the product **2**. – IR (film): $\tilde{\nu} = 1635$ cm^{-1} (C=N), 1533 (C=C), 812 (S–N). – ^{1}H NMR ($CDCl_3$): $\delta = 2.52$ (s, 3H, CH_3), 4.96 (s, 2H, CH_2), 7.21–7.70 (m, 4H, aromatic H), 8.59 (s, 2H, CH=N,

aromatic-H). – $^{13}C\{^1H\}$NMR ($CDCl_3$): δ = 18.8 (CH_3), 66.3 (CH_2), 122.1 (py-$C^{3/5}$), 125.1 (isothiazole-C^4), 136.6 (py-C^4), 149.0 (py-C^6), 153.3 (CH=N), 157.7 (py-C^2), 163.6, 167.1 (isothiazole-$C^{3/5}$). – MS (70 eV); *m/z* (%): 217 (65) [M^+], 93 (100) [CH_2py+1^+].

5-(Bromomethyl)-3-methylisothiazole (**3**): A mixture of 3.3 g (29.0 mmol) of 3,5-dimethylisothiazole[11], 10.6 g (58.0 mmol) of NBS and a few milligrams of benzoyl peroxide in 200 ml of CCl_4 was heated to reflux for 12 h. The succinimide formed was filtered off and the solvent evaporated. Purification by column chromatography [20 × 2.5 cm, silica gel (32–63 μm), petroleum ether (boiling range 40–60°C)/ethyl acetate (10:1)] afforded 2.1 g (38%) of analytically pure **3**. – ^1H NMR ($CDCl_3$): δ = 2.47 (s, 3H, CH_3), 4.67 (s, 2H, CH_2), 7.02 (s, 1H, isothiazole H). – $^{13}C\{^1H\}$NMR ($CDCl_3$): δ = 18.8 (CH_3), 21.4 (CH_2), 124.5 (isothiazole-C^4), 163.5, 167.1 (isothiazole-$C^{3/5}$). – MS (70 eV); *m/z* (%): 193 (14) [M^+], 112 (100) [M^+ – Br]. – C_5H_6BrNS (193.0): calcd. C 31.27, H 3.15, N 7.29; found C 31.00, H 3.15, N 7.17.

5-{[Bis(2-diethylamino)ethyl]aminomethyl}-3-methylisothiazole (**4**): A solution of 1.0 g (5.2 mmol) of **3**, 1.1 g (5.2 mmol) of *N,N,N',N'*-tetraethyldiethylenetriamine and an excess of triethylamine in 50 ml of Et_2O was stirred at room temp. for 1 h. The triethylamine hydrobromide was filtered off and the filtrate evaporated to dryness. The residue was taken up in petroleum ether (boiling range 40–60°C) and filtered again. After evaporation of the solvent in vacuo, 1.0 g (59%) of the product remained as a yellow oil. – IR (film): $\tilde{\nu}$ = 1535 cm^{-1} (C=C), 1383. – ^1H NMR ($CDCl_3$): δ = 1.00 (t, *J* = 7.3 Hz, 12H, CH_3), 2.45 (s, 3H, CH_3), 2.49–2.60 (m, 16H, CH_2), 3.94 (s, 2H, CH_2), 6.82 (s, 1H, isothiazole-H). – $^{13}C\{^1H\}$NMR ($CDCl_3$): δ = 11.5 (CH_2CH_3), 18.8 (CH_3), 47.2 (CH_2CH_3), 51.2 (CH_2), 52.4 (CH_2), 52.7 (CH_2), 121.2 (isothiazole-C^4), 166.7, 168.5 (isothiazole-$C^{3/5}$). – MS (70 eV); *m/z* (%): 326 (1) [M^+], 240 (10) [M^+ – CH_2NEt_2], 86 (100) [$CH_2NEt_2^+$]. – $C_{17}H_{34}N_4S$ (326.6): calcd. C 62.53, H 10.50, N 17.16; found C 63.16, H 10.70, N 17.36.

3-Methyl-5-[(2-thiomethyl)ethyl]isothiazole (**5**): A solution of 2.0 g (18.0 mmol) of 3,5-dimethylisothiazole in 20 ml of THF was added to 18.0 mmol of LDA in 20 ml of THF at –70°C. The mixture was stirred for 1.5 h at –70°C turning orange-red during that time. 5.0 g (52.0 mmol) of chloromethyl methyl sulfide was added dropwise and the color changed to dark red. After warming to room temp., the solution was left stirring overnight, then quenched with a saturated aqueous NH_4Cl solution and extracted several times with Et_2O. The combined organic phases were dried with $MgSO_4$, filtered and evaporated to dryness. Column chromatography [20 × 2.5 cm, silica gel (32–63 μm), petroleum ether (boiling range 40–60°C)/ethyl acetate (6:1)] afforded 1.7 g (54%) of the oily product. – IR (film): $\tilde{\nu}$ = 1534 cm^{-1} (C=C), 1435, 1401, 812 (S–N). – ^1H NMR ($CDCl_3$): δ = 2.15 (s, 3H, SCH_3), 2.45 (s, 3H, CH_3), 2.79 (t, *J* = 7.3 Hz, 2H, CH_2), 3.17 (t, *J* = 7.3 Hz, 2H, CH_2), 6.82 (s, 1H, isothiazole-H). – $^{13}C\{^1H\}$NMR ($CDCl_3$): δ = 15.4 (SCH_3), 18.7 (CH_3), 27.7 (SCH_2), 34.6 (CH_2), 122.7 (isothiazole-C^4), 166.4, 166.7 (isothiazole-$C^{3/5}$). – MS (70 eV); *m/z* (%): 173 (36) [M^+], 126 (20) [M^+ – SMe], 61 (100) [CH_2SMe^+]. – $C_7H_{11}NS_2$ (173.3): calcd. C 48.52, H 6.40, N 8.08; found C 48.49, H 6.47, N 7.90.

{3-Methyl-N-[2-(2-pyridyl)ethyl]isothiazol-5-carbaldimine}silver(I) Trifluoromethanesulfonate (**6**): 0.23 g (1.0 mmol) of **1** was added to a solution of 0.26 g (1.0 mmol) of AgO_3SCF_3 in 50 ml of Et_2O in the dark. The precipitate formed was filtered off, washed with ether twice and dried in vacuo to yield 0.46 g (94%) of the product **6**. – IR (KBr): $\tilde{\nu}$ = 1637 cm^{-1} (C=N), 1591 (C=C), 1480, 1447, 1260, 1178, 1035 (SO_3CF_3). – IR (Nujol): $\tilde{\nu}$ = 1258 cm^{-1}, 1162, 1029 (SO_3CF_3). – ^1H NMR ([D_6]DMSO): δ = 2.43 (s, 3H, CH_3), 3.28 (t, *J* = 6.1 Hz, 2H, CH_2), 4.03 (t, *J* = 6.1 Hz, 2H, NCH_2), 7.40–7.51 (m, 3H, aromatic H), 7.91 (t, *J* = 6.2 Hz, 1H, aromatic H), 8.51 (d, *J* = 4.4 Hz, 1H, aromatic H), 8.62 (s, 1H, CH=N). – $^{13}C\{^1H\}$NMR ([D_6]DMSO): δ = 19.6 (CH_3), 40.6 (CH_2), 61.1 (NCH_2), 123.6 (py-C^3), 125.6 (isothiazole-C^4), 128.5 (py-C^5), 139.5 (py-C^4), 151.3 (py-C^6), 156.8 (CH=N), 160.1 (py-C^2), 162.9, 169.2 (isothiazole-$C^{3/5}$). – ^{19}F NMR ([D_6]DMSO): δ = –77.0. – MS (FAB); *m/z* (%): 826 (10) [(**1**)$_2Ag_2O_3SCF_3^+$], 339 (100) [(**1**)Ag^+], 232 (20) [(**1**)$^+$]. – M.p. 190°C (dec.). – $C_{13}H_{13}AgF_3N_3O_3S_2$ (488.3): calcd. C 31.98, H 2.68, N 8.61; found C 32.03, H 2.77, N 8.64.

{3-Methyl-N-[(2-pyridyl)methyl]isothiazol-5-carbaldimine}silver(I) Trifluoromethanesulfonate (**7**): Starting from 0.22 g (1.0 mmol) of **2** the preparation was carried out analogously to the one for **6** to yield 0.38 g (80%) of the product. – IR (KBr): $\tilde{\nu}$ = 1634 cm^{-1} (C=N), 1532 (C=C), 1281, 1161, 1028 (SO_3CF_3). – IR (Nujol): $\tilde{\nu}$ = 1276 cm^{-1}, 1154, 1029 (SO_3CF_3). – ^1H NMR ([D_6]acetone): δ = 2.57 (s, 3H, CH_3), 5.27 (s, 2H, CH_2), 7.64–8.06 (m, 4H, aromatic H), 8.73 (d, *J* = 4.4 Hz, 1H, aromatic H), 9.13 (s, 1H, CH=N). – $^{13}C\{^1H\}$NMR ([D_6]acetone): δ = 19.9 (CH_3), 64.6 (CH_2), 124.6, 124.9 (py-$C^{3/5}$), 129.1 (isothiazole-C^4), 140.1 (py-C^4), 151.6 (py-C^6), 157.6, 158.9 (CH=N, py-C^2), 162.9, 171.2 (isothiazole-$C^{3/5}$). – ^{19}F NMR ([D_6]acetone): δ = –78.3. – MS (FAB); *m/z* (%): 799 (3) [(**2**)$_2Ag_2O_3SCF_3^+$], 542 (42) [(**2**)$_2Ag^+$], 325 (100) [(**2**)Ag^+]. – M.p. 150°C (dec.). – $C_{12}H_{11}AgF_3N_3O_3S_2$ (474.2): calcd. C 30.39, H 2.34, N 8.86; found C 29.91, H 2.45, N 8.36.

(5-{[Bis(2-diethylamino)ethyl]aminomethyl}-3-methylisothiazole)silver(I) Trifluoromethanesulfonate (**8**): Starting from 0.25 g (0.77 mmol) of **4** the preparation was carried out analogously to the one for **6** to yield 0.40 g (89%) of the product. – IR (KBr): $\tilde{\nu}$ = 1544 cm^{-1} (C=C), 1263, 1162, 1029 (SO_3CF_3). – ^1H NMR ([D_6]acetone): δ = 1.15 (t, *J* = 7.2 Hz, 12H, CH_3), 2.65 (s, 3H, CH_3), 2.73–2.88 (m, 16H, CH_2), 4.25 (s, 2H, CH_2), 7.53 (s, 1H, isothiazole-H). – $^{13}C\{^1H\}$NMR ([D_6]acetone): δ = 12.4 (CH_2CH_3), 19.5 (CH_3), 48.3 (CH_2CH_3), 51.1 (2 CH_2), 51.7 (CH_2), 126.4 (isothiazole-C^4), 165.8, 168.2 (isothiazole-$C^{3/5}$). – ^{19}F NMR ([D_6]acetone): δ = –78.3. – MS (FAB); *m/z* (%): 904 (12) [(**4**)Ag_2^+ + $N(CH_2CH_2NEt_2)_2$ + O_3SCF_3], 646 (10) [(**4**)Ag^+ + $N(CH_2CH_2NEt_2)_2$], 434 (100) [(**4**)Ag^+], 327 (22) [(**4**)$^+$]. – M.p. 150°C (dec.). – $C_{18}H_{34}AgF_3N_4O_3S_2$ (583.5): calcd.C 37.05, H 5.87, N 9.60; found C 36.90, H 5.98, N 9.54.

{3-Methyl-5-[(2-thiomethyl)ethyl]isothiazole}silver(I) Trifluoromethanesulfonate (**9**): Starting from 0.35 g (2.0 mmol) of **5** the preparation was carried out analogously to the one for **6** to yield 0.83 g (97%) of the product. – IR (KBr): $\tilde{\nu}$ = 1534 cm^{-1} (C=C), 1386 (C=N), 1254, 1033 (SO_3CF_3), 808 (S–N). – IR (Nujol): $\tilde{\nu}$ = 1285 cm^{-1}, 1242, 1156, 1024 (SO_3CF_3). – ^1H NMR ([D_6]DMSO): δ = 2.22 (s, 3H, SCH_3), 2.39 (s, 3H, CH_3), 2.90 (t, *J* = 7.1 Hz, 2H, CH_2), 3.22 (t, *J* = 7.1 Hz, 2H, CH_2), 7.08 (s, 1H, isothiazole-H). – $^{13}C\{^1H\}$NMR ([D_6]DMSO): δ = 16.9 (SCH_3), 19.6 (CH_3), 27.7 (SCH_2), 35.6 (CH_2), 124.4 (isothiazole-C^4), 167.4, 167.9 (isothiazole-$C^{3/5}$). – ^{19}F NMR ([D_6]DMSO): δ = –77.1. – MS (FAB); *m/z* (%): 969 (8) [(**5**)$_2Ag_3(O_3SCF_3)_2^+$], 711 (14) [(**5**)$_2Ag_2O_3SCF_3^+$], 538 (36) [(**5**)$AgO_3SCF_3^+$], 455 (22) [(**5**)$_2Ag^+$], 282 (100) [(**5**)Ag^+]. – M.p. 135°C (dec.). – $C_8H_{11}AgF_3NO_3S_3$ (430.3): calcd. C 22.34, H 2.58, N 3.26; found C 23.42, H 2.92, N 3.33.

X-ray Structure Determinations: The measurements were carried out with a Siemens P4 (Nicolet Syntex) R3m/v four-circle diffractometer with graphite-monochromated Mo-K_α radiation. All calculations were performed with a micro-vax computer using the SHELXT PLUS software package. Structures were solved by direct

methods with the SHELX 93 and SHELXS-86 programs[20]. An absorption correction (ψ scan, $\Delta\psi = 10°$) was applied to all data. Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares calculation. Table 1 compiles the data for the structure determinations. Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-405599 (**6**), -405598 (**8**) and -405600 (**9**).

Table 1. Crystal data and refinement details for complexes **6**, **8** and **9**

	6	**8**	**9**
formula	$C_{26}H_{26}Ag_2F_6N_6O_6S_4$	$C_{36}H_{68}Ag_2F_6N_8O_6S_4$	$C_{16}H_{22}Ag_2F_6N_2O_6S_6$
M_r	976.6	1167.0	860.3
crystal size [mm]	0.15 x 0.30 x 0.35	0.20 x 0.30 x 0.30	0.20 x 0.20 x 0.30
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [Å]	8.226(1)	13.369(2)	10.200(5)
b [Å]	8.674(1)	14.722(1)	11.806(3)
c [Å]	12.973(2)	13.919(2)	11.889(4)
α [°]	87.02(1)	90	87.02(3)
β [°]	75.13(1)	113.56(1)	78.82(3)
γ [°]	70.60(1)	90	79.28(3)
V [Å^3]	843.30	2511.20	1378.80
$\rho_{calcd.}$ [g cm^{-3}]	1.923	1.543	2.071
Z	1	2	2
$F(000)$ [e]	484	1200	848
T [K]	200	200	200
μ (Mo-K_α) [mm^{-1}]	1.492	1.017	1.950
scan mode	ω	ω	ω
hkl range	0–9, ±9, ±14	–12–15, –9–16, ±15	0–10, ±13, ±13
2θ range [°]	5.0–48.0	3.3–48.0	4.1–48.2
measured refl.	2849	4114	4202
obsd. refl. $I > 2\sigma(I)$	2569	3111	3379
refined parameters	233	299	350
resid. el. dens. [eÅ^{-3}]	0.580/-0.655	0.380/-0.437	0.531/-0.555
R1	0.026	0.033	0.028
wR2	0.082	0.117	0.069
Goodness-of-fit	1.415	0.797	1.003

☆ Dedicated to Prof. Dr. *Rolf Gleiter* on the occasion of his 60th birthday.

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