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Structural Features of Silver(I) and Copper(I) Bis(thiophene-2-carbaldehyde imine) Trifluoromethanesulfonate Complexes in the Solid State and in Solution: Crystal Structures of $[\text{Ag}\{\text{Th-2-CH}=\text{N}-(S)\text{-CHMePh}\}_2](\text{O}_3\text{SCF}_3)$ and $[\text{Cu}\{5\text{-Me-Th-2-CH}=\text{N-}i\text{-Pr}\}_2](\text{O}_3\text{SCF}_3)$ and a ^1H , ^{19}F , and ^{109}Ag NMR Study¹

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From the 1:2 molar reactions of $\text{M}(\text{O}_3\text{SCF}_3)$ [$\text{M} = \text{Ag}(\text{I}), \text{Cu}(\text{I})$] with the NS donor ligand system 5-R-Th-2-CH=N-R' (R = H, Me, *t*-BuMe₂Si; R' = *i*-Pr, *t*-Bu, CH₂-*t*-Bu, (S)-CHMePh) stable $[\text{M}\{5\text{-R-Th-2-CH}=\text{N-R}'\}_2](\text{O}_3\text{SCF}_3)$ complexes were obtained. X-ray crystal structures of $[\text{Ag}\{\text{Th-2-CH}=\text{N}-(S)\text{-CHMePh}\}_2](\text{O}_3\text{SCF}_3)$ and $[\text{Cu}\{5\text{-Me-Th-2-CH}=\text{N-}i\text{-Pr}\}_2](\text{O}_3\text{SCF}_3)$ have been determined. Their basic molecular structures are isostructural, showing complex cations and noncoordinating O_3SCF_3^- anions. The silver(I) compound crystallizes in space group *C*2 with a monoclinic cell of dimensions $a = 18.746$ (4) Å, $b = 12.462$ (3) Å, $c = 14.878$ (4) Å, $\beta = 119.71$ (2)°, and $Z = 4$. Each cationic complex present in the unit cell has a Δ configuration about the Ag(I) center. The copper(I) compound crystallizes in space group *P* $\bar{1}$, having a triclinic cell with $a = 10.765$ (1) Å, $b = 14.217$ (3) Å, $c = 8.694$ (2) Å, $\alpha = 101.46$ (2)°, $\beta = 90.05$ (1)°, $\gamma = 77.71$ (1)°, and $Z = 2$. The unit cell contains one pair of enantiomeric complexes, i.e. one cation having Δ and one having Λ configuration about the Cu(I) center. In both complexes, the cation structure consists of a linearly coordinated sp-hybridized metal nucleus with strong imine-N-M bonds and extremely weak thiophene-S-M interactions. The coordination geometry of the metal centers seems to be determined to a large extent by this linear N-M-N arrangement in combination with the *s*-cis conformation of the thienylmethylidene-amino skeleton, as a consequence of which the S donor atoms are directed toward the metal nucleus. ^1H and ^{19}F NMR experiments indicate that in CD_2Cl_2 solution these monocationic complexes have N-M-N arrangements similar to those found in the solid state. The group 11 metal is surrounded by two NS ligands in a pseudotetrahedral geometry, which is very flexible: intermolecular exchange processes can only be slowed down at low temperatures (<255 K) whereas intramolecular exchange processes cannot be interrupted at all, even at 130 K. The results of ^{109}Ag NMR experiments agree very well with a solution structure of the Ag(I) complexes that has this pseudotetrahedral, but predominantly linear, coordination geometry. It can be concluded that the intrinsic thiophene-S-group 11 metal interaction possesses negligible bonding character and, probably, is no more than a dipole-cation attraction.

Introduction

Recently we reported the solid-state and solution structures of a series of coordination complexes derived from $\text{Ag}^1\text{O}_3\text{SCF}_3$ or $\text{Cu}^1\text{O}_3\text{SCF}_3$ and a tetradentate ligand system (abbreviated as N_2S_2), consisting of two thienylmethylidene-amino moieties bridged by an (*R*),(*S*)-1,2-cyclohexanediy l unit.² These complexes could be isolated in a 2:2 as well as 1:2 metal to ligand ratio, $[\text{M}_2\{\text{N}_2\text{S}_2\}_2](\text{OTf})_2$ and $[\text{M}\{\text{N}_2\text{S}_2\}_2](\text{OTf})$, respectively, which are depicted schematically in Figure 1.

The 2:2 complex of silver exists in the solid state in two enantiomeric forms in which both metal nuclei have the same configuration, i.e. either Δ or Λ .³ Each Ag(I) center is four-surrounded, its coordination sphere comprising two imine nitrogen atoms well within bonding range and two more distant thiophene sulfur atoms. The low-temperature solution structure of this dinuclear silver(I) complex proves to be identical with the solid-state structure. At temperatures above 220 K the Ag-N bonds are still unaffected⁴ but the observed metal configuration becomes an averaged one due to intramolecular exchange processes. The solution structure of the corresponding dinuclear copper complex is more rigid, which can be deduced from the absence of intramolecular exchange even up to 294 K.

These results suggest a contribution of a bonding interaction between Ag(I) or Cu(I) and the thiophene sulfur atoms. Moreover, this view seems to be supported by the fact that a comparable ligand system, in which the thiophene units are replaced by phenyl groups, only yields stable silver complexes in a metal to ligand ratio of 1:2.^{2a} However, other observations are not consistent with a contribution of a M-thiophene-S bond. For instance, the 1:2 complex $[\text{M}\{\text{N}_2\text{S}_2\}_2](\text{OTf})$ is easier to isolate from equimolar solutions of ligand and metal salt than the 2:2 complex $[\text{M}_2\{\text{N}_2\text{S}_2\}_2](\text{OTf})_2$. The greater stability of the 1:2 complex is even more pronounced when the cyclohexanediy l bridging group

in the N_2S_2 ligand is replaced by an ethanediy l unit.⁵

Considering the conflicting nature of the available information, we strive to develop a better understanding of the interaction between group 11 metals having oxidation state +1 and thiophene sulfur atoms. Therefore, this paper presents an elaborate study concerning coordination complexes of $\text{Ag}^1\text{O}_3\text{SCF}_3$ and a number of NS donor ligands containing a single thienylmethylidene-amino fragment (i.e. half of the N_2S_2 ligand system), as well as some corresponding copper(I) complexes. Synthesis and characterization of both solid-state and solution structures are reported.

It was shown that Ag NMR spectroscopy can give information about the dynamic behavior of silver-containing complexes and that the chemical shift of the Ag(I) nucleus is very sensitive toward changes in its environment.^{2,6} In view of the similarity of the coordination properties of the group 11 metals,⁷ conclusions derived

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- (2) (a) van Stein, G. C.; van Koten, G.; Vrieze, K.; Spek, A. L.; Klop, E. A.; Brevard, C. *Inorg. Chem.* **1985**, *24*, 1367-1375. (b) Spek, A. L.; Duisenberg, A. J. M.; van Stein, G. C.; van Koten, G. *Acta Crystallogr., Sect. C* **1985**, *C41*, 374-377. (c) van Stein, G. C.; van Koten, G.; Blank, F.; Taylor, L. C.; Vrieze, K.; Spek, A. L.; Duisenberg, A. J. M.; Schreurs, A. M. M.; Kojic-Prodic, B.; Brevard, C. *Inorg. Chim. Acta* **1985**, *98*, 107-120.
- (3) For the meaning and use of δ/Δ and λ/Λ , see: Ernst, R. E.; O'Connor, M. J. O.; Holm, R. H. *J. Am. Chem. Soc.* **1967**, *89*, 6104-6113.
- (4) This can be deduced from the observable coupling, $^3J(\text{H-}^{107,109}\text{Ag})$, on the imine-H resonance.
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- (6) See also: (a) van Stein, G. C.; van Koten, G.; Vrieze, K.; Brevard, C.; Spek, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4486-4492. (b) van Stein, G. C.; van Koten, G.; Vrieze, K.; Brevard, C. *Inorg. Chem.* **1984**, *23*, 4269-4278. (c) van Stein, G. C.; van Koten, G.; De Bok, B.; Taylor, L. C.; Vrieze, K.; Brevard, C. *Inorg. Chim. Acta* **1984**, *89*, 29-39.
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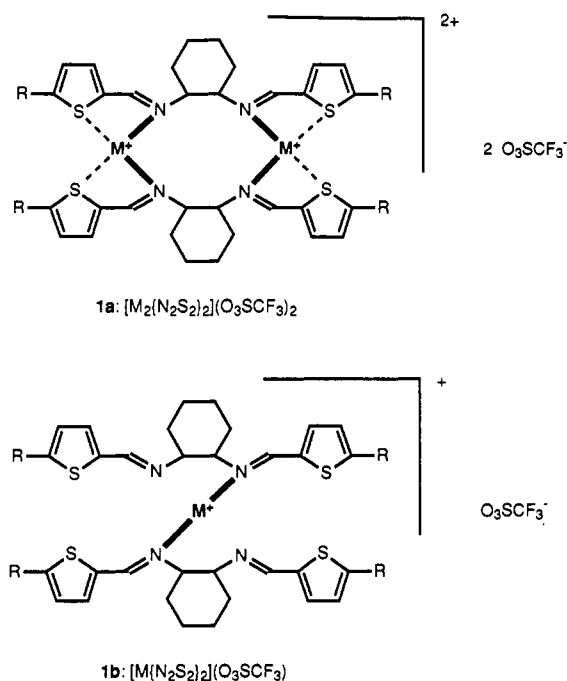
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Table I. Analytical Data (%) for $[M\{5-R-Th-2-CH=N-R'\}_2](O_3SCF_3)$ ($[M\{NS\}_2](OTf)$)

compd	R	R'	C	H	F	N	S
$[Ag\{NS1\}_2](OTf)$	H	<i>i</i> -Pr	36.27 (36.24)	3.90 (3.94)	10.15 (10.12)	5.03 (4.97)	17.25 (17.07)
$[Ag\{NS2\}_2](OTf)$	Me	<i>i</i> -Pr	38.43 (38.58)	4.41 (4.43)	9.68 (9.64)	4.70 (4.74)	16.37 (16.26)
$[Cu\{NS2\}_2](OTf)$	Me	<i>i</i> -Pr	41.83 (41.71)	4.73 (4.79)	10.48 (10.42)	5.15 (5.12)	17.45 (17.58)
$[Ag\{NS3\}_2](OTf)$	TBS	<i>i</i> -Pr	43.74 (43.98)	5.86 (6.36)	7.10 (7.20)	3.59 (3.54)	12.32 (12.14)
$[Ag\{NS4\}_2](OTf)$	H	<i>t</i> -Bu	38.23 (38.58)	4.21 (4.43)	9.46 (9.64)	4.70 (4.74)	15.23 (16.26)
$[Ag\{NS5\}_2](OTf)$	Me	<i>t</i> -Bu	40.61 (40.71)	4.88 (4.88)	9.23 (9.20)	4.53 (4.52)	15.63 (15.52)
$[Ag\{NS6\}_2](OTf)$	H	CH_2-t -Bu	40.67 (40.71)	4.92 (4.88)	9.08 (9.20)	4.51 (4.52)	15.43 (15.52)
$[Ag\{NS7\}_2](OTf)$	Me	CH_2-t -Bu	42.67 (42.66)	5.37 (5.29)	8.73 (8.81)	4.33 (4.33)	15.00 (14.85)
$[Ag\{NS8\}_2](OTf)$	H	(<i>S</i>)-CHMePh	47.12 (47.17)	3.81 (3.81)	8.30 (8.29)	4.12 (4.07)	14.13 (13.99)
$[Cu\{NS8\}_2](OTf)$	H	(<i>S</i>)-CHMePh	51.20 (50.42)	4.24 (4.07)	9.20 (8.86)	4.51 (5.36)	14.51 (14.95)
$[Ag\{NS9\}_2](OTf)$	Me	(<i>S</i>)-CHMePh	48.46 (48.67)	4.19 (4.23)	8.00 (7.97)	3.91 (3.91)	13.50 (13.44)
$[Ag\{NS10\}_2](OTf)$	TBS	(<i>S</i>)-CHMePh	51.10 (51.13)	5.84 (5.94)	6.14 (6.22)	3.08 (3.06)	10.63 (10.50)

Figure 1. Schematic representations of $[M_2\{N_2S_2\}_2](OTf)_2$ and $[M\{N_2S_2\}_2](OTf)$.

from Ag NMR data are likely to apply also to bonding features in corresponding copper(I) complexes, the latter being virtually inaccessible by $^{63,65}Cu$ NMR due to a spin quantum number $I = 3/2$ vs $I = 1/2$ for $^{107,109}Ag$.⁸ An ^{109}Ag NMR study aimed at broadening our knowledge of the phenomena governing the position and changes of the ^{109}Ag resonance values is therefore included.

The present study is part of a project to create chiral coordination complexes, whose structures are controlled by conformational constraints built in a polydentate N,N',S,S' donor ligand.⁹

Experimental Section

Preparation of the Compounds. Solvents used in the preparation were either diethyl ether and benzene, freshly distilled and stored under nitrogen atmosphere, or methanol of pa grade.

Commercially available amines, 5-R-thiophene-2-carbaldehyde ($R = H, Me$), and silver(I) trifluoromethanesulfonate were used without purification. 5-TBS-thiophene-2-carbaldehyde ($TBS = t-BuMe_2Si$) was synthesized by using a generally applicable method to obtain organosilicon-substituted thiophene derivatives¹⁰ and purified by recrystallization

from diethyl ether. Copper(I) trifluoromethanesulfonate-0.5-benzene was prepared according to ref 11.

Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

5-R-Thiophene-2-carbaldehyde Imine-R'. The ligands (abbreviated as 5-R-Th-2-CH=N-R' or NS in general) were prepared as described by Coakley et al.¹² and purified either by distillation in vacuo ($R = H$ and $R' = i$ -Pr or *t*-Bu; $R = Me$ and $R' = i$ -Pr, *t*-Bu, or CH_2-t -Bu; $R = TBS$ and $R' = i$ -Pr or (*S*)-CHMePh; Kugelrohr apparatus, boiling point range 90–130 °C at about 10 mm), affording light yellow oils, or by crystallization from diethyl ether, affording white ($R = H$; $R' = CH_2-t$ -Bu, (*S*)-CHMePh) or yellow crystals ($R = Me$; $R' = (S)$ -CHMePh).

$[Ag\{5-R-Th-2-CH=N-R'\}_2](O_3SCF_3)$. A solution of $Ag^+O_3SCF_3$ (2.0 mmol) in methanol (10 mL) was added to a solution of 5-R-Th-2-CH=N-R' (4.05 mmol) in methanol (10 mL). The reaction mixture was stirred for 30 min at room temperature, filtered through Celite, and subsequently cooled to -80 °C. Either in a direct manner or after addition of diethyl ether this procedure afforded white solids or crystals for all complexes. The products were isolated, washed twice with 5 mL of cold diethyl ether, and dried in vacuo. Yields, depending on the method used, were 50–95%.

$[Cu\{5-R-Th-2-CH=N-R'\}_2](O_3SCF_3)$. Under an atmosphere of dry nitrogen, a solution of $Cu^+O_3SCF_3 \cdot 1/2 C_6H_6$ (2.0 mmol) in benzene (30 mL) was added to a solution of 5-R-Th-2-CH=N-R' (4.05 mmol) in benzene (20 mL). The reaction mixture was stirred for 30 min at room temperature, during which a green oil separated from the solvent. For the copper complex with 5-Me-Th-2-CH=N-*i*-Pr the oil solidified upon cooling to 4 °C, affording light green crystals, which were isolated, washed with benzene (2×5 mL), and dried in vacuo, yield 75%. Despite numerous attempts the complex with Th-2-CH=N-(*S*)-CHMePh could not be crystallized. For the latter complex the benzene layer was separated by decantation and the remaining oil was concentrated in vacuo, a process affording a very viscous gel, which was used in further experiments without purification.

Analytical data of the complexes, shortly referred to as $[M\{NS\}_2](OTf)$, are presented in Table I.

Physical Measurements. 1H NMR spectra were recorded on Bruker AC100 and WM250 spectrometers with tetramethylsilane as an external reference. Where indicated, low-temperature measurements were carried out in a mixture (roughly 1:2) of CD_2Cl_2 and Freon-21. With this solvent mixture, temperatures down to 130 K could be reached without substantial loss of field homogeneity as a result of viscosity aspects. Experiments in which Freon-21 was substituted by Freon-12 (the latter having no protons at all) failed because at low temperatures the complexes proved insoluble in the resulting solvent mixture. Freon-21 and Freon-12 were both purchased from Ucar.

^{19}F NMR spectra were recorded on a Bruker AC100 spectrometer, $CFCl_3$ being used as an external reference.

^{109}Ag NMR spectra¹³ were recorded on a Bruker AC100 spectrometer, applying the INEPT pulse sequence as described by Brevard et al.¹⁴ unless denoted otherwise. $AgNO_3$ (5.9 M in D_2O) was used as an external reference.

The degree of association of $[Ag\{NS2\}_2](OTf)$ was calculated from vapor-pressure measurements with a Hewlett-Packard 320B osmometer

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- (13) Because of the 15% larger γ value, ^{109}Ag is the more suitable nucleus for NMR measurements: ^{107}Ag (51.82%) and ^{109}Ag (48.18%) both have $I = 1/2$, the γ values being -1.0828×10^7 and -1.2449×10^7 rad $T^{-1} s^{-1}$, respectively.⁸
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Table II. Crystallographic Data for [Ag{NS8}₂](OTf) and [Cu{NS2}₂](OTf)

	[Ag{NS8} ₂](OTf)	[Cu{NS2} ₂](OTf)
formula	C ₂₇ H ₂₆ AgF ₃ N ₂ O ₃ S ₃	C ₁₉ H ₂₆ CuF ₃ N ₂ O ₃ S ₃
mol wt	687.60	547.18
space group	C2	P1̄
a, Å	18.746 (4)	10.765 (1)
b, Å	12.462 (3)	14.217 (3)
c, Å	14.878 (4)	8.694 (2)
α, deg	90.00	101.46 (2)
β, deg	119.71 (2)	90.05 (1)
γ, deg	90.00	77.71 (1)
V, Å ³	3018.8 (14)	1273.0 (5)
Z	4	2
ρ _{calc} , g·cm ⁻³	1.48	1.43
μ, cm ⁻¹	9.1	11.4
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
T, °C	25	25
weighting scheme	unit weights	w = 1/(5.5 + F _o + 0.02F _o ²)
final R, R _w	0.053, -	0.053, 0.081

Table III. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for the Atoms Constituting the [M{C-S-C-C-N-C₂}]⁺ Skeletons

atom	x/a	y/b	z/c	U ^{eq} , Å ²
[Ag{NS8} ₂] ⁺				
Ag	0.58058 (6)	0.50000 (0)	0.23954 (7)	0.0762 (5)
N1	0.5897 (6)	0.6645 (9)	0.2032 (7)	0.053 (6)
N2	0.5645 (6)	0.3386 (9)	0.2818 (8)	0.058 (7)
S1	0.4224 (2)	0.5528 (4)	0.0451 (3)	0.071 (2)
S2	0.6673 (4)	0.3432 (4)	0.1693 (5)	0.109 (4)
C1	0.4467 (8)	0.6857 (12)	0.0757 (10)	0.061 (9)
C4	0.3194 (8)	0.5779 (16)	-0.0345 (11)	0.083 (11)
C5	0.5302 (8)	0.7241 (12)	0.1450 (9)	0.059 (8)
C6	0.6733 (8)	0.7104 (14)	0.2711 (10)	0.071 (9)
C14	0.6034 (9)	0.2423 (14)	0.1741 (11)	0.076 (10)
C17	0.6787 (13)	0.2747 (21)	0.0737 (13)	0.133 (18)
C18	0.5688 (8)	0.2502 (13)	0.2417 (11)	0.069 (9)
C19	0.5291 (8)	0.3339 (12)	0.3520 (10)	0.063 (9)
[Cu{NS2} ₂] ⁺				
Cu	0.09401 (7)	0.26092 (5)	0.43056 (8)	0.0494 (4)
N1	0.2209 (5)	0.2646 (4)	0.2843 (5)	0.052 (3)
N2	-0.0446 (4)	0.2608 (3)	0.5623 (5)	0.045 (3)
S1	0.2584 (2)	0.3590 (1)	0.6383 (2)	0.062 (1)
S2	0.1924 (2)	0.0825 (1)	0.5634 (2)	0.071 (1)
C1	0.3534 (5)	0.3403 (5)	0.4707 (7)	0.054 (3)
C4	0.3630 (7)	0.4152 (5)	0.7527 (8)	0.065 (4)
C6	0.3217 (6)	0.2962 (5)	0.3179 (7)	0.056 (4)
C7	0.2046 (8)	0.2239 (6)	0.1142 (8)	0.078 (5)
C10	-0.0553 (6)	0.1953 (4)	0.6381 (7)	0.051 (3)
C11	0.0411 (6)	0.1095 (4)	0.6464 (7)	0.052 (3)
C14	0.2333 (8)	-0.0234 (5)	0.6370 (8)	0.077 (5)
C16	-0.1564 (6)	0.3465 (5)	0.5765 (9)	0.065 (4)

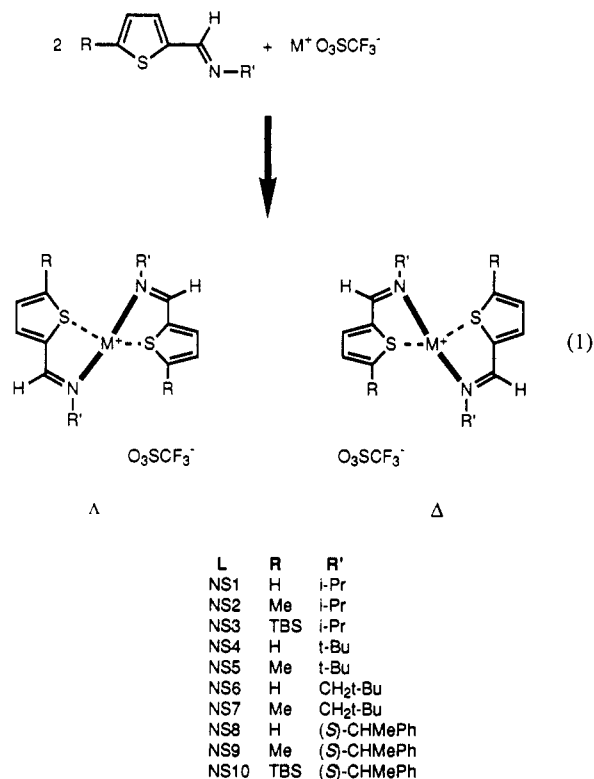
in dichloromethane. The instrumental error will be about 5%.

Data Collection and Structure Determinations of [Ag{Th-2-CH=N-(S)-CHMePh}₂](O₃SCF₃) and [Cu{5-Me-Th-2-CH=N-*i*-Pr}₂](O₃SCF₃). The crystallographic data of the complexes are summarized in Table II; fractional coordinates and equivalent isotropic parameters of selected atoms are given in Table III. The reflections were measured on a Nonius CAD4 diffractometer (25 °C, θ-2θ scan) using graphite-monochromated radiation. Those with an intensity below the 2.5σ(I) level were treated as unobserved. Refinement proceeded by means of anisotropic block-diagonal least-squares calculations. The results for the O₃SCF₃ anions are rather poor, probably due to disorder, for which no satisfactory model could be obtained. The H atoms of [Ag{NS8}₂](OTf) were not very well indicated in ΔF Fourier syntheses and have been omitted. The six non-methyl H atoms of [Cu{NS2}₂](OTf) were clearly visible in ΔF Fourier syntheses, while those of the methyl group showed disorder. Therefore, in the Cu complex only the six first mentioned H atoms have been included in the refinement with isotropic temperature parameters. Unit weights gave the most satisfactory weighting for the Ag complex. For the Cu complex a weighting scheme w = 1/(5.5 + F_o + 0.02F_o²) was employed. An empirical absorption correction (DIFABS)¹⁵ was applied.

The calculations were performed with XRAY76,¹⁶ the atomic scattering factors were taken from Cromer and Mann,¹⁷ and the dispersion correction factors were from ref 18.

Results

The 1:2 molar reactions of M(O₃SCF₃) with NS donor ligands 5-R-Th-2-CH=N-R' (referred to as NS1-NS10, see eq 1) in



either methanol [M = Ag(I)] or benzene [M = Cu(I)] afforded off-white silver(I) or light green copper(I) complexes, the latter isolable either as crystals ([Cu{NS2}₂](OTf)) or a very viscous oil ([Cu{NS8}₂](OTf)). The 1:2 metal salt-to-ligand stoichiometries are confirmed by elemental analysis. The silver(I) complexes are air stable but decompose in solution when exposed to light for prolonged periods (hours). The copper(I) complexes are very air sensitive and decompose instantly upon exposure. Both complex types have good solubilities in dichloromethane, methanol, and acetone but are insoluble in apolar solvents.

X-ray Crystal and Molecular Structures of [Ag{5-Me-Th-2-CH=N-(S)-CHMePh}₂](O₃SCF₃) and [Cu{Th-2-CH=N-*i*-Pr}₂](O₃SCF₃). The molecular geometries of both [M{NS}₂]⁺ cations and the adopted numbering scheme are shown in a PLUTO drawing (Figure 2); selected bond distances and angles are listed in Table IV.

The X-ray structure of the silver(I) complex shows that each unit cell contains four discrete, identical [Ag{NS8}₂]⁺ cations and four OTf⁻ anions. The configuration of each silver center is unique and can be designated as Λ.³ In the case of the copper(I) complex there are two discrete, enantiomeric [Cu{NS2}₂]⁺ cations, the copper ions having Δ (depicted in Figure 2) and Λ configurations, respectively, and two OTf⁻ anions per unit cell.

Analysis of the ligand skeleton conformations in the silver(I) and copper(I) complexes, reveals that in both complexes the two NS ligands coordinate to the group 11 metal center via one short imine-N bond [Ag-N1 = 2.147 (11), Ag-N2 = 2.174 (11) Å; Cu-N1 = 1.883 (5), Cu-N2 = 1.883 (5) Å]. The angle between

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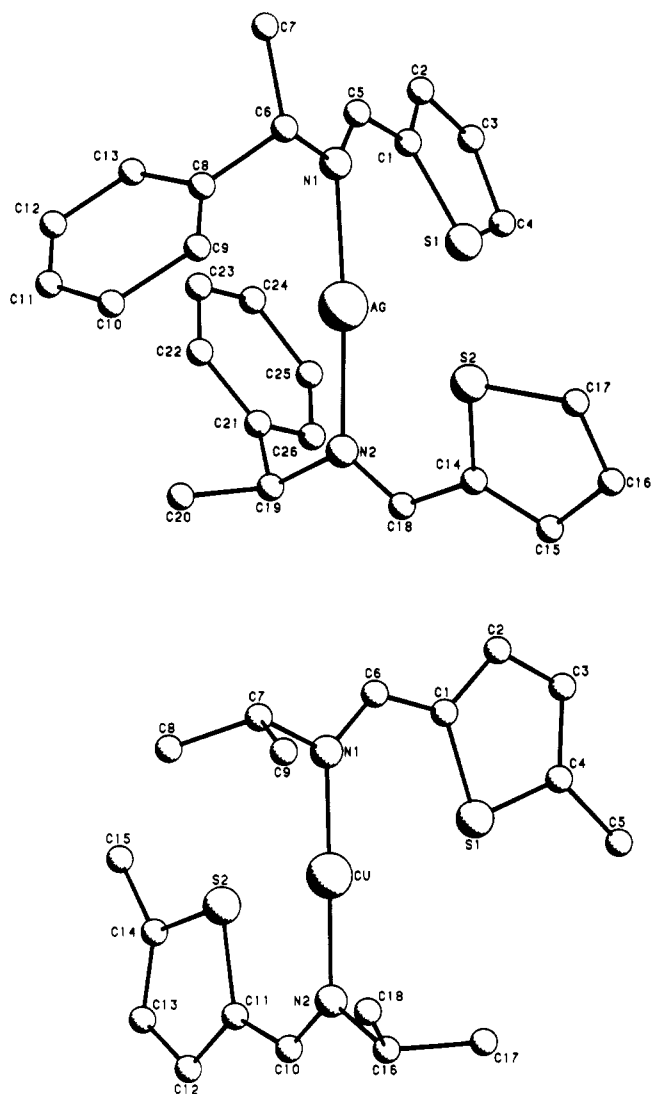


Figure 2. PLUTO drawings of $[\text{Ag}\{\text{NS}_8\}_2]^+$ and $[\text{Cu}\{\text{NS}_2\}_2]^+$. ORTEP projections are available as supplementary material.

these M–N bonds is $174.7(5)$ and $174.4(2)^\circ$ for the Ag(I) and Cu(I) complex, respectively. As evidenced by the PLUTO drawings, both ligands in either complex have an E configuration at the C=N bond. The thiophene ring systems and the CH=N moieties are more or less coplanar (Ag, -13 and 18° ; Cu, 0 and 4°) with the thiophene-imine skeleton having the s-cis conformation. Hence, the sulfur atom is in the proximity of the metal cation, but the M–S distances [Ag–S1 = $3.017(3)$, Ag–S2 = $3.036(7)$ Å; Cu–S1 = $2.895(2)$, Cu–S2 = $2.985(2)$ Å] are at best only slightly less than the maximum bond distances accepted for Ag(I)– and Cu(I)–S bonds (being 3.01 and 2.94 Å, respectively),¹⁹ thus indicating weak interactions. The S–M–S angle is $104.5(1)^\circ$ for the Ag(I) complex and $87.6(1)^\circ$ for the Cu(I) complex.

$[\text{M}\{\text{S-R-Th-2-CH=N-R'}\}_2](\text{O}_3\text{SCF}_3)$ in Solution. As in the solid state, the complexes in solution are present as cation–anion species. The ^{19}F NMR spectra of each of these complexes in CD_2Cl_2 at 298 K show one singlet ^{19}F resonance having a chemical shift value (relative to CFCl_3) from δ (ppm) -78.3 to -78.8 (Table V), a range expected for noncoordinating O_3SCF_3 .^{6a}

Mole masses for $[\text{Ag}\{\text{NS}_2\}_2](\text{OTf})$ calculated from osmometric vapor-pressure measurements in CH_2Cl_2 ($c = 14$ mmol·L⁻¹ gives $M_{\text{exp}} = 264.3$, and $c = 39$ mmol·L⁻¹ gives $M_{\text{exp}} = 323.5$) agree well, within the experimental error of about 10%, with the theoretical mole mass of 295.5 , the latter being half of the complex mass due to correction for the cation–anion nature. Hence, in

Table IV. Selected Distances (Å) and (Dihedral) Angles (deg) of the $[\text{M}\{\text{C-S-C-N-C}\}_2]^+$ Skeletons in $[\text{Ag}\{\text{NS}_8\}_2](\text{OTf})$ and $[\text{Cu}\{\text{NS}_2\}_2](\text{OTf})$

$[\text{Ag}\{\text{NS}_8\}_2]^+$		$[\text{Cu}\{\text{NS}_2\}_2]^+$	
Distances			
Ag–N1	2.147 (11)	Cu–N1	1.883 (5)
Ag–N2	2.174 (11)	Cu–N2	1.883 (5)
Ag–S1	3.017 (03)	Cu–S1	2.895 (2)
Ag–S2	3.036 (07)	Cu–S2	2.985 (2)
S1–C1	1.718 (15)	S1–C1	1.724 (7)
S1–C4	1.723 (13)	S1–C4	1.721 (8)
S2–C14	1.762 (20)	S2–C11	1.717 (6)
S2–C17	1.760 (26)	S2–C14	1.723 (8)
N1–C5	1.260 (16)	N1–C6	1.272 (8)
N1–C6	1.495 (16)	N1–C7	1.502 (8)
N2–C18	1.274 (20)	N2–C10	1.267 (9)
N2–C19	1.495 (16)	N2–C16	1.505 (7)
C1–C5	1.464 (17)	C1–C6	1.427 (9)
C14–C18	1.445 (28)	C10–C11	1.437 (8)
Angles			
N1–Ag–N2	174.7 (05)	N1–Cu–N2	174.4 (2)
S1–Ag–S2	104.5 (01)	S1–Cu–S2	87.6 (1)
N1–Ag–S1	73.3 (02)	N1–Cu–S1	79.9 (2)
N1–Ag–S2	114.0 (04)	N1–Cu–S2	105.8 (2)
N2–Ag–S1	105.5 (02)	N2–Cu–S1	104.2 (1)
N2–Ag–S2	71.3 (04)	N2–Cu–S2	78.4 (1)
C1–S1–C4	93.8 (08)	C1–S1–C1	92.2 (3)
C14–S2–C17	92.5 (11)	C11–S2–C14	92.1 (4)
Ag–N1–C5	125.7 (10)	Cu–N1–C6	125.4 (4)
C5–N1–C6	120.9 (12)	C6–N1–C7	117.6 (5)
Ag–N2–C18	127.9 (12)	Cu–N2–C10	127.1 (4)
C18–N2–C19	116.6 (13)	C10–N2–C16	116.2 (5)
S1–C1–C5	123.5 (11)	S1–C1–C6	124.3 (5)
N1–C5–C1	124.4 (13)	N1–C6–C1	125.8 (6)
S2–C14–C18	121.9 (12)	S2–C11–C10	125.4 (5)
N2–C18–C14	122.6 (16)	N2–C10–C11	125.6 (6)
Dihedral Angles			
S1–C1–C5–N1	-13	S1–C1–C6–N2	0
S2–C14–C18–N2	18	S2–C11–C10–N1	4

Table V. ^{19}F Chemical Shifts^a and ^{109}Ag NMR Data^b for $[\text{M}\{\text{NS}\}_2](\text{OTf})$

compd	R	R'	^{19}F $\delta(\text{O}_3\text{SCF}_3^-)$	^{109}Ag		
				T_c^c	T_{exp}	δ_{obs}^d
AgO ₃ SCF ₃ Complexes						
$[\text{Ag}\{\text{NS}1\}_2](\text{OTf})$	H	<i>i</i> -Pr	-78.60	180	188	526
$[\text{Ag}\{\text{NS}2\}_2](\text{OTf})$	Me	<i>i</i> -Pr	-78.65	185	200	530
					223	520
					233	520
					298	513 ^d
$[\text{Ag}\{\text{NS}3\}_2](\text{OTf})$	TBS	<i>i</i> -Pr	-78.73	255	250	533
$[\text{Ag}\{\text{NS}4\}_2](\text{OTf})$	H	<i>t</i> -Bu	-78.72	195		
$[\text{Ag}\{\text{NS}5\}_2](\text{OTf})$	Me	<i>t</i> -Bu	-78.44	200		
$[\text{Ag}\{\text{NS}6\}_2](\text{OTf})$	H	CH ₂ - <i>t</i> -Bu	-78.58	175		
$[\text{Ag}\{\text{NS}7\}_2](\text{OTf})$	Me	CH ₂ - <i>t</i> -Bu	-78.61	180		
$[\text{Ag}\{\text{NS}8\}_2](\text{OTf})$	H	(<i>S</i>)-CHMePh	-78.50	170	198	532
$[\text{Ag}\{\text{NS}9\}_2](\text{OTf})$	Me	(<i>S</i>)-CHMePh	-78.57	195	198	543
$[\text{Ag}\{\text{NS}10\}_2](\text{OTf})$	TBS	(<i>S</i>)-CHMePh	-78.76	210		
CuO ₃ SCF ₃ Complexes						
$[\text{Cu}\{\text{NS}2\}_2](\text{OTf})$	Me	<i>i</i> -Pr	-78.76			
$[\text{Cu}\{\text{NS}8\}_2](\text{OTf})$	H	(<i>S</i>)-CHMePh	-78.29			

^a CD_2Cl_2 , $T = 298$ K, δ vs CFCl_3 . ^b CD_2Cl_2 , $T = T_{\text{exp}}$ (K), δ vs AgNO_3 . ^c $T_c = {}^3J(\text{H}_{\text{im}}-{}^{107,109}\text{Ag})$ coalescence temperature (K). ^d Observed directly.²¹

solution there are two ligands per silver(I) ion.

^1H NMR data of the ligands and the $[\text{M}\{\text{NS}\}_2](\text{OTf})$ complexes have been obtained in CD_2Cl_2 (Table VI). Compared with the spectra of the free ligands, those of the complexes show downfield shifts for all resonances, notably the imine-H singlet.

A NOESY experiment with $[\text{Ag}\{\text{NS}2\}_2]^+$ at 298 K shows clearly through-space interactions for H_{im} and *i*-Pr H_α and for H_{im} and thiophene H(3). This indicates that (at least in part of the ligands present) the E configuration at the C=N bond is retained and that the thienylmethylidene fragment is coplanar

(19) Covalent radii (Å): Ag, 1.59; Cu, 1.52; S, 1.02.¹⁸ Add the usual tolerance of 0.40 Å.

Table VI. ^1H NMR Data (δ) for the Free NS Ligands and the $[\text{M}\{\text{NS}\}_2]^+$ Complex Cations^a

compd	R	R'	H _{im}	H(3)	H(4)	H _R	H _{R'}
NS1	H	<i>i</i> -Pr	8.38 s	7.38 d	7.07 dd	7.29 d (H(5))	3.51 se (H _α), 1.24 d (H _β)
Ag{NS1} ₂ ⁺			8.95 s	7.81 d	7.24 dd	7.60 d (H(5))	4.03 se (H _α), 1.42 d (H _β)
NS2	Me	<i>i</i> -Pr	8.27 s	7.07 d	6.73 d	2.48 s (H _α)	3.47 se (H _α), 1.26 d (H _β)
Ag{NS2} ₂ ⁺			8.81 s	7.62 d	6.93 d	2.50 d (H _α)	3.98 se (H _α), 1.41 d (H _β)
Cu{NS2} ₂ ⁺			8.68 s	7.62 d	6.91 d	2.49 d (H _α)	3.95 se (H _α), 1.45 d (H _β)
NS3	TBS	<i>i</i> -Pr	8.40 s	7.34 d	7.22 d	0.32 s (H _β), 0.95 s (H _γ)	3.50 se (H _α), 1.23 d (H _β)
Ag{NS3} ₂ ⁺			8.90 s	7.78 d	7.32 d	0.19 s (H _β), 0.77 s (H _γ)	4.01 se (H _α), 1.42 d (H _β)
NS4	H	<i>t</i> -Bu	8.40 s	7.38 d	7.09 dd	7.33 d (H(5))	1.30 s (H _β)
Ag{NS4} ₂ ⁺			8.74 s	7.77 d	7.26 dd	7.58 d (H(5))	1.52 s (H _β)
NS5	Me	<i>t</i> -Bu	8.29 s	7.10 d	6.74 d	2.49 s (H _α)	1.28 s (H _β)
Ag{NS5} ₂ ⁺			8.75 s	7.70 d	6.92 d	2.48 s (H _α)	1.52 s (H _β)
NS6	H	CH ₂ - <i>t</i> -Bu	8.32 s	7.39 d	7.08 dd	7.30 d (H(5))	3.32 s (H _α), 0.98 s (H _β)
Ag{NS6} ₂ ⁺			8.59 s	7.74 d	7.24 dd	7.60 d (H(5))	3.69 s (H _α), 1.08 s (H _β)
NS7	Me	CH ₂ - <i>t</i> -Bu	8.20 s	7.09 d	6.74 d	2.49 s (H _α)	3.28 s (H _α), 0.96 s (H _β)
Ag{NS7} ₂ ⁺			8.48 s	7.56 d	6.92 d	2.50 s (H _α)	3.64 s (H _α), 1.07 s (H _β)
NS8	H	(<i>S</i>)-CHMePh	8.49 s	7.45 d	7.10 dd	7.35 d (H(5))	4.55 q (H _α), 7.3 m (H _β); 1.61 d (H _β)
Ag{NS8} ₂ ⁺			8.94 s	7.76 d	7.17 dd	7.45 d (H(5))	4.89 q (H _α), 7.30 s (H _β), 1.66 d (H _β)
Cu{NS8} ₂ ⁺			8.91 s	7.58 d	7.11 dd	7.4 d (H(5))	4.91 q (H _α), 7.30 s (H _β), 1.69 d (H _β)
NS9	Me	(<i>S</i>)-CHMePh	8.35 s	7.11 d	6.75 d	2.50 s (H _α)	4.47 q (H _α), 7.3 m (H _β), 1.55 d (H _β)
Ag{NS9} ₂ ⁺			8.80 s	7.57 d	6.85 d	2.40 s (H _α)	4.85 q (H _α), 7.30 s (H _β), 1.69 d (H _β)
NS10	TBS	(<i>S</i>)-CHMePh	8.45 s	7.3 d	7.25 d	0.34 s (H _β), 0.97 s (H _γ)	4.52 q (H _α), 7.4 m (H _β), 1.59 d (H _β)
Ag{NS10} ₂ ⁺			8.81 s	7.69 d	7.25 d	0.12 s (H _β), 0.15 s (H _β), 0.72 s (H _γ)	4.82 q (H _α), 7.33 s (H _β), 1.65 d (H _β)

^aCD₂Cl₂, *T* = 298 K, δ vs Me₃Si; s = singlet, d = doublet, q = quartet, se = septet, and m = multiplet.

with an *s*-cis conformation, thus having the sulfur in proximity of the Ag(I) center; a COSY experiment has been carried out to ascertain these interpretations.

The spectra are to some extent temperature dependent, but pattern changes are minimal upon cooling, apart from a broadening of the signals as a result of increasing viscosity of the solvent. Only in the case of the silver(I) complexes is there a marked change for the imine-H singlet appearing as a doublet in the slow-exchange limit of the intermolecular exchange processes. The temperature at which this pattern change takes place (the coalescence temperature *T_c*; see Table V) strongly depends on the R and R' substituents: a quite clear positive correlation can be observed between the coalescence temperature and the bulkiness of R as well as the degree of substitution of R'-C_α (disregarding R' = (*S*)-CHMePh, which deviates slightly). The splitting of the imine-H resonance is due to $^3J(^1\text{H}-^{107,109}\text{Ag})$, having a magnitude of about 15 Hz, as was proven by selective decoupling of the ¹⁰⁹Ag isotope in the case of [Ag{NS9}₂]⁺, which resulted in a badly resolved but, nevertheless, tripletlike pattern; this indicates that the imine N is coordinating to the Ag(I) center. The appearance of the coupled imine-H signal is a doublet rather than a doublet of doublets because of the γ -value ratio of ¹⁰⁷Ag and ¹⁰⁹Ag of 1.14 in combination with the small $^3J(^1\text{H}-^{107,109}\text{Ag})$.¹³ Even at very low temperatures the imine-H resonances of the copper(I) complexes still appear as singlets because couplings with either ⁶³Cu or ⁶⁵Cu are not resolved as a result of the large quadrupole moments of both isotopes ($I = 3/2$).²⁰

Although it is highly likely that these 1:2 complexes in solution possess a metal nucleus surrounded by four donor atoms, as is found for the solid-state structure (vide supra), the ¹H NMR data do not provide clues as to the exact coordination geometry about the group 11 metal center. Possibilities include a pure four-coordinated geometry in which both NS ligands are chelate bonded via imine-N and thiophene-S lone pairs and a four-surrounded yet two-coordinated one as a result of monodentate imine-N coordination; the latter geometry may appear as a four-coordinated one when the NS ligands, the thienylmethylidene unit in the *s*-cis conformation, are restricted in a chelatelike fashion. An intermediate form, being a three-coordinated geometry with one chelate- and one monodentate-bonded ligand, can be excluded, since the resulting NMR pattern with nonequivalent NS ligands is never observed. A rigid four-surrounded coordination geometry, i.e. four-coordination or restricted, pseudo-chelate-bonded two-coordination, implies that the metal center has either Δ or Λ configuration; it is this situation that might be identified by ¹H

NMR spectroscopy if prochiral or chiral groups are present in the ligand system.

Therefore, we investigated [M{NS}₂]⁺ cations with R' = *i*-Pr ([Ag{NS2}₂]⁺, [Cu{NS2}₂]⁺, [Ag{NS3}₂]⁺) or (*S*)-CHMePh ([Ag{NS9}₂]⁺, [Ag{NS10}₂]⁺) in more detail. In the intramolecular slow-exchange limit, the *i*-Pr methyl groups will be diastereotopic, thus giving rise to two anisochronous methyl doublets in the spectra. Furthermore, the presence of the chiral N-substituent (*S*)-CHMePh may result in two possible diastereomeric complex forms, i.e. $\Delta(S)(S)$ and $\Lambda(S)(S)$, each having its own ¹H resonance pattern. However, even at 130 K, in a mixture of CD₂Cl₂ and Freon-21, the ¹H NMR spectra present no evidence of diastereomer formation with R' = (*S*)-CHMePh nor do they show diastereotopic methyl groups when R' = *i*-Pr; in the latter case only a relative broadening of the *i*-Pr methyl pattern can be observed.

¹⁰⁹Ag NMR Spectroscopy of [Ag{5-R-Th-2-CH=N-R'}₂](O₃SCF₃). Silver complexes with NS ligands having R = H, Me, or TBS and R' = *i*-Pr or (*S*)-CHMePh have been investigated in more detail by ¹⁰⁹Ag NMR spectroscopy (for data, see Table V).

In or near the slow-exchange limit of the intermolecular exchange processes, i.e. near or below the coalescence temperature (*T_c*) when the rupture of the imine-N-Ag bond is slow or blocked on the NMR time scale, the presence of $^3J(^1\text{H}-^{109}\text{Ag})$ on the imine-H resonance permits measuring the chemical shift values of the ¹⁰⁹Ag ion via the INEPT (insensitive nuclei enhanced by polarization transfer) pulse sequence.¹⁴ At higher temperatures, above the intermediate-exchange region, the proton-silver coupling is lost and ¹⁰⁹Ag data can only be obtained by direct measurement.²¹ Because *T_c* in general is rather low, it proved to be very difficult to have a workable complex concentration to perform the experiments. Hence, the ¹⁰⁹Ag chemical shift value of [Ag{NS3}₂]⁺ is the only one actually measured in the slow-exchange limit. The other data are obtained near the slow-exchange limit in the intermediate-exchange region, and one experiment is run in the fast-exchange situation at room temperature. Nevertheless some general observations can be made.

All resonances are found in the relatively narrow range of 513 to 543 ppm. A clear trend is an increase in chemical shift, i.e. a deshielding effect, upon lowering the experimental temperature. It seems that the sensitivity of the observed δ value toward changes in temperature is maximal near *T_c* and that at more elevated temperatures the resonance converges to a single value. Com-

(20) Marker, A.; Gunther, M. J. *J. Magn. Reson.* **1982**, *47*, 118-132.

(21) 10-mm tube, 1.2 g of complex in 2.2 mL of CD₂Cl₂, acquisition time 0.33 s, delay time 300 s, and 790 scans.

paring values obtained for $[\text{Ag}\{\text{NS}_2\}_2]^+$ (below T_c) and $[\text{Ag}\{\text{NS}_2\}_2]^+$ (very near T_c) shows that the difference is rather small.

Discussion

To our knowledge, Coakley et al. were the first to report a study on the coordination behavior of ligand systems that contain one thienylmethylidene-amino unit (abbreviated as 5-R-Th-2-CH=N-R' or NS) toward group 11 and metal ions.¹² They suggested that their complex made of copper(II) dichloride and Th-2-CH=N-Me, with an $\text{M}\{\text{NS}\}_2$ stoichiometry, possessed an N_2S_2 donor set as a result of chelate-bonded ligands. Yamada and co-workers showed however, by means of IR spectroscopy, that in these copper(II) and also in copper(I) (di)halide complexes the metal center was coordinated by imine nitrogen atoms (i.e. monodentate coordinated NS ligands) and bridging halide anions.²² Corresponding silver(I) complexes have not been reported before.

$[\text{M}\{5\text{-R-Th-2-CH=N-R'}\}_2](\text{O}_3\text{SCF}_3)$ in the Solid State. The crystal structures of $[\text{Ag}\{\text{NS}_2\}_2](\text{OTf})$ and $[\text{Cu}\{\text{NS}_2\}_2](\text{OTf})$ consist of discrete $[\text{M}\{\text{NS}_2\}_2]^+$ cations and OTf^- anions. Corrected for the difference in the ionic radii of Ag(I) and Cu(I), the structures of both $[\text{M}\{\text{NS}_2\}_2]^+$ cations have a very high similarity. In either monocation the M-imine-N distance is short [Ag-N = 2.16 Å (av); Cu-N = 1.88 Å (av)], indicating a strong bond. Within the experimental error the N-M-N angles are identical, i.e. 174.6° (av). The M-thiophene-S distances of Ag-S = 3.02 and Cu-S = 2.94 Å (av) are both very long compared to literature values for M(I)-thioether-S bonds, e.g. Ag(I), 2.49–2.60 Å,^{7a,9,23} and Cu(I), 2.32–2.33 Å,^{7a} suggesting at best a weak interaction. Only the S-M-S angles of both complexes differ considerably, being 104.5 (1) and 87.6 (1)° for Ag(I) and Cu(I), respectively.

The above data indicate an almost perfectly linear hybridization of the metal(I) center. For d^{10} nuclei like Ag(I) and Cu(I) this linearity can be rationalized in terms of sp hybridization, either hybrid having a substantial overlap with an imine-N lone pair as evidenced by the short M-N distances. The remaining empty perpendicular p orbitals are available to interact with thiophene-S lone pairs. Accordingly, the S-M-S angle would be expected to be close to 90°. This apparent M-thiophene-S interaction however seems to be no reason in itself for the observed geometry but most probably is a consequence of the structure of the ligand. Calculations show that a free thienylmethylidene-amino structure having an E configuration at the imine double bond and a coplanar thiophene and imine fragment as a result of π conjugation is a global minimum on the potential energy surface, the *s-cis* conformation being slightly more stable than the *s-trans* conformation.²⁴ Since the latter conformation is disfavored in the complex because of the accompanying repulsive interaction between thiophene H(3) and the metal nucleus, coordination of the imine-N lone pair in a ligand with an *s-cis* conformation inevitably brings the thiophene sulfur in the proximity of the metal center.

In the copper(I) complex the S-Cu-S angle is close to 90°, but in the silver(I) complex there is a relatively large deviation from this ideal value, which can be interpreted as a sign that a possible M-S interaction only plays a minor role. CPK molecular model studies suggest that this deviation is a result of strain caused by the ligand's rather bulky R' group, (S)-CHMePh. This strain, however, would be even bigger if the cation would have the Δ configuration. The fact that the found Λ configuration is energetically favored strongly supports the assumption of van Stein and van Koten et al. that in the comparable cation-anion complex $[\text{M}\{5\text{-R-Pyr-2-CH=N-(S)-CHMePh}\}_2](\text{O}_3\text{SCF}_3)$ [M = Ag(I), Cu(I); R = H, Me], in which the thienyl unit of the ligand is substituted by a pyridyl one, the most abundant diastereomer in solution also possesses the Λ configuration.^{6c}

With comparison of the $[\text{Ag}\{\text{NS}_2\}_2]^+$ monocation to the dicationic 2:2 silver(I) complex $[\text{Ag}_2\{\text{N}_2\text{S}_2\}_2]^{2+}$ (see Figure 1; for a

detailed description, see ref 2c), it is clear that the Ag(I) centers of both complexes indeed have a similar local environment. The imine-N-Ag distances are short and almost identical in both complexes, ranging from 2.15 to 2.17 Å. The N-Ag-N angle in the monocation is slightly closer to linear than those in the dication: i.e. 174.5 (5)° vs 169.1° (av), respectively. Although shorter in the dication the thiophene-S-Ag distances are still long, being 2.92–2.99 Å in $[\text{Ag}_2\{\text{N}_2\text{S}_2\}_2]^{2+}$ vs 3.02 Å in $[\text{Ag}\{\text{NS}_2\}_2]^+$, representing only weak or absent bonds. The S-Ag-S angles, however, differ considerably: 104.7 (1)° in the monocation vs 82.1° (av) in the dication. The subtle differences in the structures of the mono- and dication seem to arise from the presence of the (R)(S)-1,2-cyclohexanediyl unit in the dication, its specific shape causing a less linear coordination geometry and a slightly smaller silver-thiophene-sulfur distance.

$[\text{M}\{5\text{-R-Th-2-CH=N-R'}\}_2](\text{O}_3\text{SCF}_3)$ in Solution. From the ¹⁹F NMR data and vapor-pressure measurements it can be concluded that in solution the complexes are completely dissociated into $[\text{M}\{\text{NS}_2\}_2]^+$ cations and OTf^- anions.

Variable-temperature ¹H NMR data indicate that the structure of the cationic species $[\text{M}\{\text{NS}_2\}_2]^+$ in CD_2Cl_2 solution is very flexible on the NMR time scale. However, the skeletons of the coordinated NS ligands remain rather rigid, even at 298 K, as evidenced by the NOESY experiment, comprising an E configuration at the C=N bond in combination with a coplanar imine function and thiophene ring in the *s-cis* conformation, i.e. the sulfur atom residing in the proximity of the metal nucleus.

At 298 K the silver(I) complexes are prone to intermolecular exchange processes, since no silver coupling can be detected on the proton resonances. With lowering of the temperature to 255 K and below, depending on the R and R' substituents of the ligand, these intermolecular exchange processes become slow, as evidenced by the change of the imine-H resonance pattern from a singlet to a doublet due to ³J(¹H-¹⁰⁷Ag), as was established by a heteronuclear ¹H-¹⁰⁹Ag decoupling experiment. This indicates that the imine-N-Ag(I) bond dissociation is slow on the NMR time scale. For the corresponding copper(I) complexes it is not possible to determine with certainty whether intermolecular exchange processes are taking place in CD_2Cl_2 solution because ³J(¹H-^{63,65}Cu) is not resolved. As copper(I) complexes are generally more stable than their silver(I) counterparts,²⁵ it is likely that the slow-exchange limit of the intermolecular exchange processes involving N-Cu dissociation is reached at a higher temperature than in the case of the corresponding silver(I) complexes.

¹H NMR experiments with (pro)chiral ligand containing complexes clearly show that intramolecular exchange processes cannot be slowed down substantially for either Ag(I) or Cu(I), implying a fast configuration inversion at the M(I) center. Only the relative broadening of the *i*-Pr methyl resonance pattern at very low temperatures suggests an intermediate exchange, which can be interpreted as evidence for the four-surrounded coordination geometry in solution.

Nevertheless, the combined structural data for the $[\text{M}\{\text{NS}_2\}_2](\text{OTf})$ complexes in solution are consistent with the pseudotetrahedral yet linearly hybridized, two-coordinated geometry formed by M(I) bonded to two imine-N and two thiophene-S atoms in its proximity due to the rigidity of the ligand skeleton.

With comparison of the structural features of the mononuclear $[\text{M}\{\text{NS}_2\}_2](\text{OTf})$ and the dinuclear $[\text{M}_2\{\text{N}_2\text{S}_2\}_2](\text{OTf})_2$, it seems that the possibility of stabilizing the configuration at the metal centers in the 2:2 complex is entirely due to the specific shape of the (R)(S)-1,2-cyclohexanediyl unit present in the N_2S_2 ligand and not the result of a thiophene-S-M interaction. This hypothesis is supported by our observation that upon substitution of (R)(S)-1,2-cyclohexanediyl for a 1,2-ethanediyl unit, fixation of the metal center configuration is no longer possible. The fact that with a ligand system comparable to N_2S_2 , in which the thienyl group is substituted for a phenyl one, only complexes having a 1:2 stoichiometry can be isolated^{2c} can be explained by a resulting

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strong repulsive interaction between phenyl H(3) and the metal center if the 2:2 complex would be formed.

^{109}Ag NMR Spectroscopy of $[\text{Ag}\{5\text{-R-Th-2-CH=N-R}'\}_2](\text{O}_3\text{SCF}_3)$. Lowering of the temperature results in a decrease of the intermolecular exchange rate of the ligands and thus an increase of the ligand's influence on the Ag(I) center. The observed trend, being an increase in the Ag chemical shift implying a more deshielded nucleus, is in total agreement with this reasoning.

In CD_2Cl_2 solution, the observed $\delta(^{109}\text{Ag})$ only varies between 513 and 543 ppm. Spanning only about 20 ppm, the influence on the chemical shift position of either slow or fast ligand exchange is apparently a lot less than the actual basic structure of the complexes, the latter being responsible for a shift of over 500 ppm relative to the standard. Apart from some difference in exchange rates at a given temperature, solvents do not seem to have an influence on the chemical shift position (cf. values measured by the authors for $[\text{Ag}\{\text{NS}\}_2]^+$ in CD_3OD of δ 520 ppm at 178 K and 504 ppm at 298 K). Therefore, the found data range may well be compared with data reported by Endo et al.²⁶ for a number of silver complexes in aqueous solutions. These workers established a broad chemical shift range from roughly 200 to 1200 ppm, in which generally the linearly coordinated complexes occupy the high-field sector up to 500 ppm and the tetrahedrally coordinated ones the low-field sector starting at 600 ppm. This puts our complexes at the outer edge of the linear two-coordinated family, bordering the tetrahedral complexes, which is in close agreement with their putative solution structure.

Considering the size of $\Delta\delta(^{109}\text{Ag})$ upon reaching T_c , it is possible to predict the δ value in the slow-exchange limit. It is striking to note that all the values seem to converge to a single value that only slightly depends on R' and apparently not at all on the nature of R: complexes with R' = *i*-Pr will resonate at about 535 ppm, while those with R' = (S)-CHMePh have $\delta(^{109}\text{Ag})$ at about 545 ppm. This small difference in $\delta(^{109}\text{Ag})$ may well be due to structural and not to electronic influences associated with R', since there is a good correlation with the distortion of the complex's linear coordination when R' = (S)-CHMePh, evidenced by a lower T_c than expected on basis of C_a 's degree of substitution (vide supra), resulting in a slightly increased tetrahedral tendency. Thus, in spite of the postulated sensitivity of the Ag resonance frequency toward subtle changes in its environment, the influence of either R or R' in complexes of the type $[\text{Ag}\{\text{NS}\}_2]^+$ seems to be negligible.

Although various other experiments show the dicationic complexes $[\text{Ag}_2\{\text{N}_2\text{S}_2\}_2]^{2+}$ to be four-surrounded but two-coordinated, the ^{109}Ag chemical shifts of 678 ppm measured for R = H and 659 ppm for R = Me^{2c} characterize these compounds as weakly tetrahedrally coordinated, according to the distribution found by Endo et al. Apparently there is a kind of twilight zone in the ^{109}Ag chemical shift range where linearly hybridized but strongly four-surrounded and weakly tetrahedrally coordinated coincide. It is clear, though, that the dicationic complexes possess a more prominent tetrahedral character, due to the presence of the

bridging (R)(S)-1,2-cyclohexanediyl, which forces the thiophene-S lone pairs toward the metal center, than the monocationic $[\text{Ag}\{\text{NS}\}_2]^+$ complexes presented in this paper. The marked sensitivity difference of $\delta(^{109}\text{Ag})$, obtained for $[\text{Ag}\{\text{NS}\}_2]^+$ or $[\text{Ag}_2\{\text{N}_2\text{S}_2\}_2]^{2+}$, toward the substituent at the thiophene 5-position, R, remains unclear.

Conclusions

From the 1:2 molar reactions of $\text{M}(\text{O}_3\text{SCF}_3)$ [M = Ag(I), Cu(I)] with the NS donor ligand system 5-R-Th-2-CH=N-R' (R = H, Me, *t*-BuMe₂Si; R' = *i*-Pr, *t*-Bu, CH₂-*t*-Bu, (S)-CHMePh), stable $[\text{M}\{5\text{-R-Th-2-CH=N-R}'\}_2](\text{O}_3\text{SCF}_3)$ complexes were obtained.

X-ray crystal structure determinations of representative silver(I) and copper(I) complexes have established the cation-anion nature of these compounds, the cation structure consisting of a linearly coordinated sp-hybridized metal nucleus with strong imine-N-M bonds and extremely weak thiophene-S-M interactions. The coordination geometry of the metal centers seems to be determined to a large extent by this linear N-M-N arrangement in combination with the *s*-cis conformation of the thienylmethylidene-amino skeleton, as a consequence of which the S donor atoms are directed toward the metal nucleus.

^1H and ^{19}F NMR experiments indicate that in CD_2Cl_2 solution these monocationic complexes have N-M-N arrangements similar to those found in the solid state. The group 11 metal is surrounded by two NS ligands in a pseudotetrahedral geometry, which is very flexible: intermolecular exchange processes can only be slowed down at low temperatures (<255 K) whereas intramolecular exchange processes cannot be interrupted at all, even at 130 K.

^{109}Ag NMR spectroscopy has proven to be a valuable tool to investigate the nature of the Ag(I) center in these complexes. Although there is conflicting information concerning the sensitivity of the frequency toward subtle structural changes, in general the magnitude of the chemical shift can be correlated with the basic coordination geometry.

It can be concluded that if steric constraints force a thiophene-S donor atom and group 11 metal cationic center together, some weak bonding interaction might be induced, as is shown by the $[\text{M}_2\{\text{N}_2\text{S}_2\}_2]^{2+}$ dication. In this complex the (R),(S)-1,2-cyclohexanediyl bridging groups of both ligands apparently preorganize the conformation to form a kind of cavity with an N₂S₂ donor atom array, suited to accommodate a metal cation. However, the intrinsic thiophene-S-group 11 metal interaction possesses negligible bonding character, as established for the monocationic $[\text{M}\{\text{NS}\}_2]^+$, and is probably no more than a dipole-cation attraction.

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Supplementary Material Available: ORTEP figures and tables of full crystallographic data, fractional atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles (13 pages); tables of structure factors (16 pages). Ordering information is given on any current masthead page.

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