

# Dinuclear Silver(I) and Copper(I) Complexes with Neutral N<sub>2</sub>S<sub>2</sub> Donor Ligands and their Reactivities Towards CO. Structures in Solution (<sup>1</sup>H and INEPT <sup>109</sup>Ag NMR) and in the Solid (X-ray) of [Ag<sub>2</sub>{μ-(R)(S)-1,2-(thiophene-2-CH=N)<sub>2</sub>-cyclohexane}<sub>2</sub>](O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>

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## Abstract

The 1/1 reactions of the neutral N<sub>2</sub>S<sub>2</sub> donor system (R)(S)-1,2-(5-R-thiophene-2-CH=N)<sub>2</sub>-cyclohexane (R = H, **1a** or Me, **1b**) with [M(O<sub>3</sub>SCF<sub>3</sub>)] [M = Ag(I) or Cu(I)] yielded ionic complexes, consisting of a dinuclear [M<sub>2</sub>(1)<sub>2</sub>]<sup>2+</sup> dication and O<sub>3</sub>-SCF<sub>3</sub><sup>-</sup> monoanions.

An X-ray crystallographic study characterized the molecular structure of [Ag<sub>2</sub>-(**1a**)<sub>2</sub>](O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>, in the monoclinic unit cell, space group P2<sub>1</sub>/n, with Z = 4; a = 17.26(1), b = 15.08(2), c = 19.960(17) Å, β = 106.15(4)°, V = 4991 Å<sup>3</sup>. The structure was refined to R is 0.0704. The two N<sub>2</sub>S<sub>2</sub> ligands coordinate to the silver(I) centres in a bridging dibidentate manner with short Ag-N(imine) [e.g. Ag(1)-N(2), 2.152(10); Ag(1)-N(7), 2.162(9); Ag(2)-N(3), 2.153(10); Ag(2)-N(6), 2.158(10) Å] and long Ag-S(thiophene) distances [Ag(1)-S(1), 2.961(4); Ag(1)-S(8), 2.938(4); Ag(2)-S(4), 2.928(4); Ag(2)-S(5), 2.995(5) Å]. The Ag(1)-Ag(I) separation is 2.909(1) Å.

In solution the coordination properties of the N<sub>2</sub>S<sub>2</sub> ligands to silver(I) and copper(I) have been studied by <sup>1</sup>H and INEPT <sup>109</sup>Ag NMR spectroscopy. The <sup>1</sup>H NMR data revealed, by the presence of two thiophene-imine <sup>1</sup>H patterns at 190 K, that at this temperature i) the structural features found for [Ag<sub>2</sub>(**1a**)<sub>2</sub>]<sup>2+</sup> in the solid are retained in solution and ii) the silver(I) and copper(I) complexes have similar

structures in solution. Furthermore, the presence of <sup>3</sup>J(<sup>1</sup>H-<sup>107,109</sup>Ag) on the imine-H resonances of the silver(I) complexes indicates that at 190 K intermolecular exchange processes are slow on the NMR time scale. From the difference in δ<sup>109</sup>Ag of the [Ag<sub>2</sub>(1)<sub>2</sub>](O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub> complexes, R = H (δ + 678) or Me (δ + 659), it was concluded that weak thiophene-S-Ag(I) interactions are present, and stabilize the formation of the [M<sub>2</sub>(1)<sub>2</sub>]<sup>2+</sup> dications.

However, in the reversible reactions of [Cu<sub>2</sub>(1)<sub>2</sub>](O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub> with carbon monoxide the thiophene-S-Cu(I) bonds dissociate and neutral complexes are formed having a [{CuCO(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>}{μ-1}<sub>2</sub>] type of structure. In these complexes both the carbon monoxide and OSO<sub>2</sub>CF<sub>3</sub> groups are terminally coordinated to Cu(I) (R = H, ν(CO), 2089 cm<sup>-1</sup>; R = Me, ν(CO) = 2087 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>).

## Introduction

To understand the bonding features and reactivities of copper(I) sites in biological macromolecules the study of the coordination chemistry of copper(I) salts with polydentate ligands has become an important research area [1]. In a previous paper [2] we have pointed out that when a rationale is given for the reactivities of the Cu(I) sites in coordination complexes in solution, based on conformational and configurational features, it is particularly important to know the exact nature in solution of the metal coordination sphere. For this reason we are studying not only the solution structures of copper(I) complexes with polydentate ligands by

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$^1\text{H}$  NMR but also those of the corresponding silver(I) complexes. Both silver(I) isotopes  $^{107}\text{Ag}$  (51.82%) and  $^{109}\text{Ag}$  (48.18%) have  $I = 1/2$  and therefore  $\nu_J(^1\text{H}-^{107,109}\text{Ag})$  in the  $^1\text{H}$  NMR spectra of the silver(I) complexes can be detected when intermolecular exchange processes are slow on the NMR time scale [3]. Furthermore,  $^{109}\text{Ag}$  NMR data, obtained by direct  $^{109}\text{Ag}$  NMR measurements, may give important information concerning the bonding features of the polydentate ligand, since  $^{109}\text{Ag}$  chemical shifts are sensitive to even small stereochemical changes in the ligand skeleton [2].

Recently we have reported a detailed study of the bonding features of the copper(I) and silver(I) complexes with the neutral  $\text{N}_4$  donor ligand system (*R*)(*S*)-1,2-(6-*R*-py-2-CH=N)<sub>2</sub>-cyclohexane (*R* = H or Me) in the solid as well as in solution [2–4]. These complexes could only be obtained in a 1/1 metal salt-to-ligand ratio and have  $[\text{M}_2(\text{N}_4)_2]^{2+}(\text{O}_3\text{SCF}_3)_2^-$  (Fig. 1) structures. To study the influence of the nature of the donor sites on the coordination properties of these types of polydentate ligands we have investigated the bonding features of the  $\text{N}_2\text{S}_2$  ligand system (*R*)(*S*)-1,2-(5-*R*-thiophene-2-CH=N)<sub>2</sub>-cyclohexane (*R* = H or Me, see Fig. 1). This  $\text{N}_2\text{S}_2$  ligand system, containing two 'inner' imine N atoms and two 'outer' thiophene-S sites, was selected in order to minimize the differences in coordination properties, caused by conformational changes [4], relative to those of the above mentioned  $\text{N}_4$ -system.

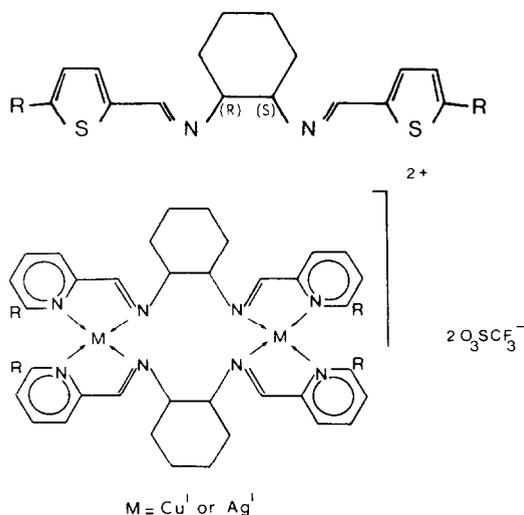


Fig. 1. Schematic representation of the  $\text{N}_2\text{S}_2$  ligand system (*R*)(*S*)-1,2-(5-*R*-thiophene-2-CH=N)<sub>2</sub>-cyclohexane (*R* = H, **1a** or Me, **1b**) (top), and of the  $[\text{M}_2(\text{N}_4)_2](\text{O}_3\text{SCF}_3)_2$  [*M* = Ag(I) or Cu(I)] complexes (bottom).

In contrast to the  $\text{N}_4$  ligands, the  $\text{N}_2\text{S}_2$  system can produce (depending on the *M*/ $\text{N}_2\text{S}_2$  ratio) with  $[\text{M}(\text{O}_3\text{SCF}_3)]$  [*M* = Ag(I) or Cu(I)] either dinuclear

$[\text{M}_2(\text{N}_2\text{S}_2)_2](\text{O}_3\text{SCF}_3)_2$  or mononuclear  $[\text{M}(\text{N}_2\text{S}_2)_2](\text{O}_3\text{SCF}_3)$  [5] complexes. Another striking difference is the fact that while the dinuclear  $[\text{Cu}_2(\text{N}_4)_2](\text{O}_3\text{SCF}_3)_2$  complexes are kinetically very stable and do not react with  $\text{H}_2\text{O}$  or CO the  $[\text{Cu}_2(\text{N}_2\text{S}_2)_2](\text{O}_3\text{SCF}_3)_2$  complexes react very easily with these small molecules.

We report in this paper the syntheses of the novel  $[\text{M}_2(\text{N}_2\text{S}_2)_2](\text{O}_3\text{SCF}_3)_2$  complexes and their characterization in the solid state by using the X-ray structure of the silver(I) complex with 5-*R* = H and in solution from  $^1\text{H}$  and  $^{109}\text{Ag}$  NMR data. Furthermore, a comparison is made between the molecular structures of the  $[\text{Ag}_2(\text{N}_2\text{S}_2)_2]^{2+}$  and the already reported  $[\text{Ag}_2(\text{N}_4)_2]^{2+}$  [2] dications.

The characterization of the Cu-CO complexes which are formed from the reversible reactions of the  $[\text{Cu}_2(\text{N}_2\text{S}_2)_2](\text{O}_3\text{SCF}_3)_2$  complexes with carbon monoxide are also included in this paper.

## Experimental

### Physical Measurements

Infrared (IR) spectra were measured on a Perkin-Elmer 283 spectrophotometer either as KBr pellets (data in Table I) or in  $\text{CH}_2\text{Cl}_2$  to obtain the solution  $\nu(\text{CO})$  data of  $[\{\text{CuCO}(\text{OSO}_2\text{CF}_3)\}_2(\mu\text{-N}_2\text{S}_2)_2]$  complexes.

Field desorption (FD) mass spectra were obtained with a Varian MAT 711 double focussing mass spectrometer equipped with a combined EI/FI/FD ion source and coupled to a spectro-system MAT 100 data acquisition unit [8]. The samples were loaded onto the emitter with the dipping technique [9]. (FD mass data are listed in Table II).

Hydrogen-1 spectra were recorded on Bruker WM 250 and AM 400 spectrometers with tetramethylsilane (TMS) as reference (see Table IV).

INEPT  $^{109}\text{Ag}$  NMR experiments were recorded in  $\text{CD}_2\text{Cl}_2$  on a Bruker WM 250 spectrometer. The procedure for obtaining these spectra is described in a previous paper [2]. For the  $^{109}\text{Ag}$  NMR data (see Results)  $\text{AgNO}_3$  (2M in  $\text{D}_2\text{O}$ ) was used as external reference.

Fluorine-19 NMR data were obtained with a Varian XL-100 (C.W.) apparatus with  $\text{CFCl}_3$  as external reference in  $\text{CD}_2\text{Cl}_2$  at 190 K (see Results).

### Preparation of the Compounds

All reactions, unless otherwise stated, were carried out under a nitrogen atmosphere using freshly distilled solvents. The  $\text{N}_2\text{S}_2$  ligands (*R*)(*S*)-1,2-(5-*R*-thiophene-2-CH=N)<sub>2</sub>-cyclohexane (*R* = H, **1a**; *R* = Me, **1b**) were prepared according to the method described in a previous paper [5]. Silver(I) trifluoromethanesulfonate and 3-methylbenzaldehyde

TABLE I. Infrared Data of the Silver(I) and Copper(I) Complexes<sup>a</sup>.

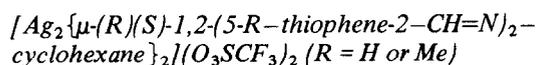
Complexes	$\nu_4(E)\nu SO_3$	$\nu_1(A_1)\nu SO_3$	$\nu_5(E)\delta SO_3$
$[Ag_2(1a)_2](O_3SCF_3)_2$	1263vs	1031s	634s
$[Ag_2(1b)_2](O_3SCF_3)_2$	1266vs	1025s	632s
$[Cu_2(1a)_2](O_3SCF_3)_2$	1270vs	1027s	632s
$[Cu_2(1b)_2](O_3SCF_3)_2$	1263vs	1027s	632s
$[\{CuCO(OSO_2CF_3)\}_2\{\mu-1a\}_2]$	1296vs 1240vs	1026s	633s
$[\{CuCO(OSO_2CF_3)\}_2\{\mu-1b\}_2]$	1293vs 1240vs	1029s	631s
$[Ag(2)_2](O_3SCF_3)$	1260vs	1031s	632s

<sup>a</sup>In KBr:  $cm^{-1}$ .TABLE II. F.D.-M.S. Data of the Silver(I) and Copper(I)<sup>a</sup> Complexes.

Complexes	Emitter Current (mA)	Species	M/Z (rel. int.)
$[Ag_2(1a)_2](O_3SCF_3)_2$	10	$\{Ag(1a)\}^+$	409(100), 410(28), 411(94), 412(17).
$[Ag_2(1b)_2](O_3SCF_3)_2$	10	$\{Ag(1b)\}^+$	437(68), 438(25), 439(100), 440(14).
$[Cu_2(1a)_2](O_3SCF_3)_2$	10	$\{Cu(1a)\}^+$	365(100), 366(28), 367(70), 368(17).
	15	$[Cu_2(1a)_2O_3SCF_3]^+$	879(100), 880(33), 881(80), 882(16), 883(15).
	22	$[Cu_2(1a)_2(O_3SCF_3)_2]^+$	1028(100), 1029(28), 1030(75), 1031(19), 1032(15).
$[Cu_2(1b)_2](O_3SCF_3)_2$	10	$[Cu_2(1b)_2]^{2+}$	393(90), 393.5(4), 394(63), 394.5(10), 395(100), 395.5(19).
	12	$[Cu_2(1b)_2O_3SCF_3]^+$	935(82), 936(33), 937(100), 938(35), 939(17), 940(8).
	15	$\{Cu(1b)O_3SCF_3\}^+$	542(100), 543(62), 544(20), 545(48), 546(12), 547(5).
$[Ag(2)_2](O_3SCF_3)$	10	$\{Ag(2)_2\}^+$	743(91), 744(39), 745(100), 746(39).

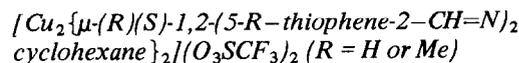
<sup>a</sup>The Cu-CO complexes  $[\{CuCO(OSO_2CF_3)\}_2\{\mu-1\}_2]$  show identical patterns to those found for the  $[Cu_2(1)_2](O_3SCF_3)_2$  complexes.

hyde are commercially available. Copper(I) trifluoromethanesulfonate  $\cdot 1/2C_6H_6$  was prepared as described in ref. 6. Pure (R)(S)-1,2-diaminocyclohexane was separated from the commercially available mixture of *cis*-[(R)(S)] and *trans*-[(R)(R), (S)(S)] isomers by the method described in ref. 7. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, T.N.O., Utrecht (The Netherlands).



To a solution of  $[Ag(O_3SCF_3)]$  (2.05 mmol) in methanol (40 mL) was added a solution of the  $N_2S_2$  ligand **1a** or **1b** (2 mmol) in methanol (40 mL). The reaction mixture was stirred for 15 min. In order to remove small excess of free  $[Ag(O_3SCF_3)]$  the solution was filtered through celite. White and pale yellow solids were obtained for  $[Ag_2(1a)_2](O_3SCF_3)_2$  and  $[Ag_2(1b)_2](O_3SCF_3)_2$

respectively by evaporation of the solvent. Pure crystals of  $[Ag_2(1a)_2](O_3SCF_3)_2$  were obtained from slow evaporation of a  $CH_2Cl_2$  solution. Anal. data: Calcd. for  $C_{17}H_{18}AgF_3N_2O_3S_3$  (R = H); C, 36.50; H, 3.24; F, 10.19; N, 5.01. Found: C, 36.57; H, 3.43; F, 10.00; N, 5.06. Calcd. for  $C_{19}H_{22}AgF_3N_2O_3S_3$  (R = Me); C, 38.85; H, 3.77; F, 9.70; N, 4.77. Found: C, 38.74; H, 3.95; F, 9.85; N, 4.55.



Addition of a solution of **1a** or **1b** (2.0 mmol) in benzene (30 mL) to a solution of  $[Cu(O_3SCF_3)] \cdot 1/2C_6H_6$  (2.0 mmol) in benzene (30 mL), resulted in the precipitation of the light yellow complexes. This mixture was stirred for 30 min and then the solvent decanted. The precipitates were washed with benzene and dried *in vacuo* at 330 K. Yields of  $[Cu_2(1)_2](O_3SCF_3)_2$  were 80–90%. Anal. data: Calcd. for:  $C_{17}H_{18}CuF_3N_2O_3S_3 \cdot 1/4C_6H_6$  (R = H):

C, 41.56; H, 3.68; F, 10.66; N, 5.24. Found: C, 41.28; H, 3.44; F, 10.87; N, 4.80. Calcd. for:  $C_{19}H_{22}CuF_3N_2O_3S_3 \cdot 1/4C_6H_6$  (R = Me): C, 43.76; H, 4.21; F, 10.13; N, 4.98. Found: C, 43.50; H, 4.45; F, 10.03; N, 4.93.

$[CuCO(OSO_2CF_3)]_2[\mu-(R)(S)-1,2-(5-R-thiophene-2-CH=N)_2-cyclohexane]_2$  (R = H or Me)

A solution of light yellow  $[Cu_2(I)_2](O_3SCF_3)_2$  (0.2 mmol) in  $CH_2Cl_2$  (20 mL) was held under a CO atmosphere (1.5 bar). After a few minutes the solution became colourless. White solids which precipitated after adding a CO saturated pentane solution were filtered off and then dried with a stream of CO. Yields of the Cu-CO complexes were 95–100%. Anal. data: Calcd. for:  $C_{18}H_{18}CuF_3N_2O_4S_3$  (R = H): C, 39.81; H, 3.34; F, 10.49; N, 5.16. Found: C, 39.45; H, 3.30; F, 10.23; N, 5.05. Calcd. for:  $C_{20}H_{22}CuF_3N_2O_4S_3$  (R = Me): C, 42.06; H, 3.88; F, 9.98; N, 4.90. Found: C, 41.59; H, 4.03; F, 9.52; N, 4.83.

$(R)(S)-1,2-(3-Me-benzene-CH=N)_2-cyclohexane$  (2)

The  $N_2$  donor ligand **2** was prepared by the method described for the  $N_2S_2$  ligand system **1** (cf. ref. 5). Reaction of 20 mmol of 3-Me-benzaldehyde and 10 mmol of  $(R)(S)-1,2$ -diaminocyclohexane in diethyl ether resulted in the formation of **2** which was isolated in an almost quantitative yield.

$[Ag\{(R)(S)-1,2-(3-Me-benzene-CH=N)_2-cyclohexane\}_2](O_3SCF_3)$

To a solution of  $[Ag(O_3SCF_3)]$  (2.0 mmol) in methanol (20 mL) a solution of the  $N_2$  ligand **2** (4.0 mmol) in methanol (20 mL) was added. The reaction mixture was stirred for a few minutes after which the solvent was evaporated. The white solid obtained was washed with diethyl ether (3 × 10 mL) to remove excess free ligand.  $[Ag(2)_2](O_3SCF_3)$  was thus obtained in almost quantitative yield. Anal. data: Calcd. for:  $C_{45}H_{52}AgF_3N_4O_3S$ : C, 60.47; H, 5.86; F, 6.38; N, 6.27. Found: C, 60.42; H, 5.99; F, 6.33; N, 6.25.

*Data Collection and Structure Determination of  $[C_{17}H_{18}AgF_3N_2O_3S_3]_2 \cdot xCH_2Cl_2$*

Single crystal data were collected on an ENRAF-NONIUS CAD4F diffractometer using Zr-filtered  $MoK\alpha$  radiation ( $\mu = 12 \text{ cm}^{-1}$ ) in the  $\omega/2\theta$  scan mode. The cell dimensions of the monoclinic unit cell, space group  $P2_1/n$ , are  $a = 17.26(1)$ ,  $b = 15.08(2)$ ,  $c = 19.960(7)$  Å,  $\beta = 106.15(4)^\circ$ ,  $V = 4991 \text{ Å}^3$  and  $Z = 4$ . The intensities of 7471 reflections up to  $\theta = 23^\circ$  were collected. A severe, approximately linear, decay requiring an intensity correction factor of 1.52 at the end of the data

collection was observed as monitored by two reference reflections (113 and 113) and indicated visually by the change of the colour of the crystal from transparent colourless to black. The diffraction data were corrected for the decay, Lorentz and polarization effects but not for absorption (a psi-scan for the close to axial reflection 122 showed a variation in the intensity of less than 10%). The structure was solved by standard Patterson and Fourier methods and refined by blocked full matrix least-squares techniques\* (SHELX-76 [10]). One of the  $O_3SCF_3^-$  anions turned out to be disordered and was included in the refinements with a disorder model [11]. In addition, the structure was found to contain large voids outside the areas that are occupied by the anions and cations. A difference electron density map clearly indicated significant residual density in those areas which were interpreted as enclosed  $CH_2Cl_2$  molecules. Their presence is also indicated by the difference between the observed density of  $1.69 \text{ g cm}^{-3}$ , as found by flotation in a mixture of n-heptane and 1,2-dibromoethane, and the density of  $1.49 \text{ g cm}^{-3}$  calculated on the basis of four  $[Ag_2(1a)_2]^{2+}$  dications and eight  $O_3SCF_3^-$  anions. Occupancy factors for the  $CH_2Cl_2$  molecules on two sites converged to 0.87 and 0.77 respectively. The resulting density of 1.67 is in agreement with the observed value. Convergence was reached at  $R = 0.0704$  for 4593 observed reflections with  $I > 2.5\sigma(I)$ . Hydrogen atoms were introduced on calculated positions and refined in the riding mode on their carrier atoms. Scattering factors were those of Cromer and Mann [12], dispersion corrections were taken from Cromer and Liberman [13]. All calculations were carried out on either a DG-Eclipse S/230 mini-computer or on a CYBER-175 of the University of Utrecht.

## Results

The 1/1 complexes  $[M_2(N_2S_2)_2](O_3SCF_3)_2$  [ $M = Ag(I)$  or  $Cu(I)$ ] of the  $N_2S_2$  donor ligands  $(R)(S)-1,2-(5-R-thiophene-2-CH=N)_2-cyclohexane$  (R = H, **1a** or Me, **1b**) were obtained by reactions of equimolar mixtures of **1a** or **1b** with either  $[Ag(O_3SCF_3)]$  or  $[Cu(O_3SCF_3)] \cdot 1/2C_6H_6$  in methanol or benzene respectively. The elemental analytical data are in agreement with an 1/1  $N_2S_2$  ligand-to-metal salt ratio in the complexes.

Infrared (I.R.) spectra of all the  $[M_2(N_2S_2)_2](O_3SCF_3)_2$  complexes, taken as KBr pellets, showed the characteristic pattern for  $O_3SCF_3^-$  anions with  $C_{3v}$  symmetry [2] (see Table I). Accordingly, the

\*Tables of positional and thermal parameters, of observed and calculated structure factors and a complete list of bond lengths and bond angles are available on request from the author (A.L.S.).

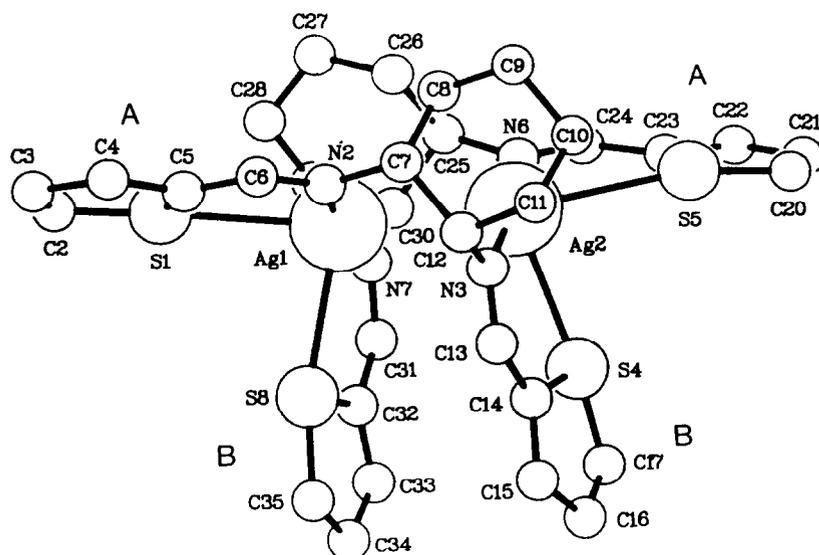


Fig. 2. PLUTO drawing of the  $[Ag_2(1a)_2]^{2+}$  dication. Hydrogen atoms are omitted for clarity. Ag---Ag distance is 2.909(1) Å.

$O_3SCF_3^-$  groups do not coordinate to the metal-IB centres. The complexes have ionic  $[M_2(1)_2]^{2+}2(O_3SCF_3)^-$  structures.

Field desorption (F.D.) mass spectrometric measurements of the complexes (see Table II) did not provide data on which conclusions could be based concerning their aggregation state. The spectra of the silver(I) complexes show only one fragment which corresponds to mononuclear  $[Ag(N_2S_2)]^+$  cations. This result contrasts with the known dinuclear structure of  $[Ag_2(1a)_2](O_3SCF_3)_2$ , which was established by X-ray methods. The spectra of the copper(I) complexes show patterns for various species with intensities which depend on the emitter current, e.g. the most abundant fragments observed when 5-R = H are  $[Cu(1a)]^+$  (10 mA),  $[Cu_2(1a)_2-O_3SCF_3]^+$  (15 mA) and  $[Cu_2(1a)_2(O_3SCF_3)_2]^+$  (22 mA) while the fragments for the complex with 5-R = Me are  $[Cu_2(1b)_2]^{2+}$  (10 mA),  $[Cu_2(1b)_2-O_3SCF_3]^+$  (12 mA) and  $[Cu(1b)O_3SCF_3]^+$  (15 mA). When it is assumed, based on the dinuclear structure of the silver(I) complex (5-R = H) in the solid, that all complexes have a dinuclear  $[M_2(1)_2]^{2+}2(O_3SCF_3)^-$  type of structure, these results indicate that the silver(I) complexes dissociate especially easily into mononuclear  $[Ag(1)]^+$  fragments in the mass spectrometer.

The silver(I) complexes are air and water stable, but they become dark upon exposure to day light for prolonged periods (weeks). The silver(I) complexes have good solubilities in acetone, methanol, dichloromethane and chloroform, but are insoluble in apolar solvents. The copper(I) complexes are air stable but react easily with water. Because of the ready hydrolyses the structural features and reactivities of these complexes with carbon monoxide have been studied in dry dichloromethane.

*X-ray Crystal and Molecular Structure of  $[Ag_2\{\mu\text{-}(R/S)\text{-}1,2\text{-}(\text{thiophene-}2\text{-CH=N})_2\text{-cyclohexane}\}_2](O_3SCF_3)_2 \cdot 1.6CH_2Cl_2$*

The crystal structure of  $[Ag_2(1a)_2](O_3SCF_3)_2$  consists of four discrete  $[Ag_2(1a)_2]^{2+}$  dications, with twofold non-crystallographic axial symmetry, together with eight  $O_3SCF_3^-$  monoanions and approximately 6.56  $CH_2Cl_2$  molecules of crystallization in the unit cell. The molecular geometry of the  $[Ag_2(1a)_2]^{2+}$  dication and the adopted numbering scheme are shown in a PLUTO drawing (Fig. 2).

In the dication each of the two  $N_2S_2$  ligands **1a** coordinates to two silver(I) centres in a bridging manner. Each Ag(I) centre is coordinated by two imine-N atoms of separate ligands with short Ag-N distances: i.e., Ag(1)-N(2), 2.152(10); Ag(1)-N(7), 2.162(9); Ag(2)-N(3), 2.153(10); Ag(2)-N(6), 2.158(10) Å. The N-Ag-N angles are close to values expected for linear ( $\sim 180^\circ$ ) coordination geometries around the silver(I) centres, i.e. N(2)-Ag(1)-N(7),  $169.1(4)^\circ$  and N(3)-Ag(2)-N(6),  $169.0(4)^\circ$ . The long Ag-S distances indicate that if there are Ag-S interactions then these must be weak [Ag(1)-S(1), 2.961(4); Ag(1)-S(8), 2.938(4), Ag(2)-S(4), 2.928(4), Ag(2)-S(5), 2.995(4) Å]. The PLUTO drawing shows that both ligands in the  $[Ag_2(1a)_2]^{2+}$  dication have two different (thiophene-2-CH=N) moieties, A and B. The two A moieties are well-separated from each other whereas the B moieties are parallel positioned. Fig. 3 shows one of the two enantiomeric forms present in the unit cell, i.e. the one in which both Ag(I) centres have the  $\Delta^*$  configuration. The distance between the two silver(I) centres is 2.909(1) Å.

\*For the abbreviations  $\delta$ ,  $\lambda$  and  $\Delta$ ,  $\Lambda$  see ref. 14.

TABLE III. Relevant Bond Lengths (Å) and Bond Angles (°) of  $[\text{Ag}_2(\mathbf{1a})_2](\text{O}_3\text{SCF}_3)_2$ .

Bond lengths (Å)							
Ag(1)···Ag(2)	2.909(1)	Ag(1)–S(1)	2.961(4)	Ag(1)–S(8)	2.938(4)	Ag(1)–N(2)	2.152(10)
Ag(1)–N(7)	2.162(9)	Ag(2)–S(4)	2.928(4)	Ag(2)–S(5)	2.995(5)	Ag(2)–N(3)	2.153(10)
Ag(2)–N(6)	2.158(10)	S(1)–C(2)	1.684(16)	S(1)–C(5)	1.728(14)	S(4)–C(14)	1.716(13)
S(4)–C(17)	1.711(16)	S(5)–C(20)	1.708(19)	S(5)–C(23)	1.718(15)	S(8)–C(32)	1.744(13)
S(8)–C(35)	1.704(16)	N(2)–C(6)	1.328(17)	N(2)–C(7)	1.439(16)	N(3)–C(12)	1.501(15)
N(3)–C(13)	1.284(17)	N(6)–C(24)	1.261(16)	N(6)–C(25)	1.465(16)	N(7)–C(30)	1.472(16)
N(7)–C(31)	1.299(15)	C(2)–C(3)	1.345(24)	C(3)–C(4)	1.405(23)	C(4)–C(5)	1.392(21)
C(5)–C(6)	1.384(19)	C(7)–C(8)	1.534(19)	C(7)–C(12)	1.540(18)	C(8)–C(9)	1.507(20)
C(9)–C(10)	1.520(24)	C(10)–C(11)	1.503(23)	C(11)–C(12)	1.541(19)	C(13)–C(14)	1.444(19)
C(14)–C(15)	1.382(19)	C(15)–C(16)	1.392(22)	C(16)–C(17)	1.358(22)	C(20)–C(21)	1.331(27)
C(21)–C(22)	1.400(23)	C(22)–C(23)	1.365(21)	C(23)–C(24)	1.443(19)	C(25)–C(26)	1.572(19)
C(25)–C(30)	1.536(17)	C(26)–C(27)	1.526(21)	C(27)–C(28)	1.527(23)	C(28)–C(29)	1.489(22)
C(29)–C(30)	1.567(18)	C(31)–C(32)	1.421(18)	C(32)–C(33)	1.366(19)	C(33)–C(34)	1.393(21)
C(34)–C(35)	1.348(24)						

Bond angles (°)					
Ag(2)–Ag(1)–S(1)	169.3(1)	Ag(2)–Ag(1)–S(8)	105.1(1)	Ag(2)–Ag(1)–N(2)	94.4(3)
Ag(2)–Ag(1)–N(7)	74.8(2)	S(1)–Ag(1)–S(8)	83.4(1)	S(1)–Ag(1)–N(2)	77.0(3)
S(1)–Ag(1)–N(7)	114.0(2)	S(8)–Ag(1)–N(2)	104.5(3)	S(8)–Ag(1)–N(7)	77.7(3)
N(2)–Ag(1)–N(7)	169.1(4)	Ag(1)–Ag(2)–S(4)	105.8(1)	Ag(1)–Ag(2)–S(5)	169.6(1)
Ag(1)–Ag(2)–N(3)	74.2(3)	Ag(1)–Ag(2)–N(6)	95.6(3)	S(4)–Ag(2)–S(5)	80.8(1)
S(4)–Ag(2)–N(3)	78.0(3)	S(4)–Ag(2)–N(6)	101.6(3)	S(5)–Ag(2)–N(3)	115.6(3)
S(5)–Ag(2)–N(6)	75.0(3)	N(3)–Ag(2)–N(6)	169.0(4)	Ag(1)–S(1)–C(2)	178.0(5)
Ag(1)–S(1)–C(5)	88.1(5)	C(2)–S(1)–C(5)	92.5(7)	Ag(2)–S(4)–C(14)	87.6(4)
Ag(2)–S(4)–C(17)	173.3(6)	C(14)–S(4)–C(17)	91.5(7)	Ag(2)–S(5)–C(20)	167.6(7)
Ag(2)–S(5)–C(23)	87.6(5)	C(20)–S(5)–C(23)	91.2(8)	Ag(1)–S(8)–C(32)	86.9(44)
Ag(1)–S(8)–C(35)	167.1(6)	C(32)–S(8)–C(35)	91.5(7)	Ag(1)–N(2)–C(6)	120.2(8)
Ag(1)–N(2)–C(7)	121.0(8)	C(6)–N(2)–C(7)	118.7(10)	Ag(2)–N(3)–C(12)	125.2(8)
Ag(2)–N(3)–C(13)	120.0(9)	C(12)–N(3)–C(13)	114.8(10)	Ag(2)–N(6)–C(24)	123.2(8)
Ag(2)–N(6)–C(25)	119.1(8)	C(24)–N(6)–C(25)	117.7(10)	Ag(1)–N(7)–C(30)	125.0(7)
Ag(1)–N(7)–C(31)	120.1(8)	C(30)–N(7)–C(31)	114.9(10)	S(1)–C(2)–C(3)	112.2(11)
C(2)–C(3)–C(4)	113.6(15)	C(3)–C(4)–C(5)	112.1(14)	S(1)–C(5)–C(4)	109.6(11)
S(1)–C(5)–C(6)	125.2(11)	C(4)–C(5)–C(6)	125.0(13)	N(2)–C(6)–C(5)	129.2(12)
N(2)–C(7)–C(8)	112.6(11)	N(2)–C(7)–C(12)	112.1(10)	C(8)–C(7)–C(12)	113.7(10)
C(7)–C(8)–C(9)	111.5(12)	C(8)–C(9)–C(10)	111.9(13)	C(9)–C(10)–C(11)	111.4(13)
C(10)–C(11)–C(12)	113.2(12)	N(3)–C(12)–C(7)	114.2(10)	N(3)–C(12)–C(11)	108.3(10)
C(7)–C(12)–C(11)	109.8(11)	N(3)–C(13)–C(14)	127.9(12)	S(4)–C(14)–C(13)	125.5(9)
S(4)–C(14)–C(15)	111.1(10)	C(13)–C(14)–C(15)	123.4(12)	C(14)–C(15)–C(16)	112.4(13)
C(15)–C(16)–C(17)	113.2(14)	S(4)–C(17)–C(16)	111.8(12)	S(5)–C(20)–C(21)	113.5(13)
C(20)–C(21)–C(22)	111.1(16)	C(21)–C(22)–C(23)	114.6(15)	S(5)–C(23)–C(22)	109.7(11)
S(5)–C(23)–C(24)	124.0(10)	C(22)–C(23)–C(24)	126.2(13)	N(6)–C(24)–C(23)	127.4(12)
N(6)–C(25)–C(26)	110.0(10)	N(6)–C(25)–C(30)	113.5(10)	C(26)–C(25)–C(30)	113.6(10)
C(25)–C(26)–C(27)	110.1(12)	C(26)–C(27)–C(28)	113.0(13)	C(27)–C(28)–C(29)	111.7(13)
C(28)–C(29)–C(30)	113.8(11)	N(7)–C(30)–C(25)	114.5(10)	N(7)–C(30)–C(29)	110.2(10)
C(25)–C(30)–C(29)	108.8(10)	N(7)–C(31)–C(32)	127.4(11)	S(8)–C(32)–C(31)	125.8(10)
S(8)–C(32)–C(33)	109.0(10)	C(31)–C(32)–C(33)	125.5(12)	C(32)–C(33)–C(34)	114.8(14)
C(33)–C(34)–C(35)	112.0(14)	S(8)–C(35)–C(34)	112.7(12)		

 $[\text{M}_2(\mathbf{1})_2](\text{O}_3\text{SCF}_3)_2$  [ $M = \text{Ag(I)}$  or  $\text{Cu(I)}$ ] in Solution

In solution the  $[\text{M}_2(\mathbf{1})_2](\text{O}_3\text{SCF}_3)_2$  complexes are, as in the solid state, present as dication-anion species. The  $^{19}\text{F}$  NMR spectra of these complexes in  $\text{CD}_2\text{Cl}_2$  at 190 K showed one singlet  $^{19}\text{F}$  resonance having chemical shift values (relative to  $\text{CFCl}_3$ ) within the range expected for non-coordinating

$\text{O}_3\text{SCF}_3^-$ ; i.e.  $\delta(\text{ppm}) -78.5^*$  for  $[\text{Ag}_2(\mathbf{1a})_2](\text{O}_3\text{SCF}_3)_2$ ;  $-78.4$  for  $[\text{Ag}_2(\mathbf{1b})_2](\text{O}_3\text{SCF}_3)_2$  and  $-78.6$  for the copper(I) complexes  $[\text{Cu}_2(\mathbf{1})_2](\text{O}_3\text{SCF}_3)_2$ .

\*A positive  $\delta$  corresponds to a higher resonance frequency ('deshielding') with respect to the reference frequency.

The coordination properties of the ligands in the dications have been studied by  $^1H$  and INEPT  $^{109}Ag$  NMR.

The  $^1H$  NMR spectra taken in  $CD_2Cl_2$  at 190 K of the silver(I) and copper(I) complexes,  $[M_2(1)_2](O_3SCF_3)_2$ , showed two resonance patterns for the 5-R-thiophene and the imine-H atoms (see Table IV and Fig. 3). The assignment of these resonances to two distinct 5-R-thiophene-2-CH=N moieties (denoted A and B in Table IV) was based on  $^1H$  homonuclear decoupling experiments. Because of the presence of small  $^4J(^1H-^1H)$  couplings ( $<1$  Hz) between the imine-H and thiophene-H-3 resonances as well as between the 5-CH<sub>3</sub> and thiophene-H-4 atoms it was possible to assign the imine-H signals at low field in the spectra of the  $[M_2(1)_2]^{2+}$  dications as well as the 5-CH<sub>3</sub> signals at low field in the spectra of the  $[M_2(1b)_2]^{2+}$  dications to the low field thiophene-H pattern (A). It appears that on complexation of the ligands with the metal IB centres the  $^1H$  resonances of the thiophene-imine moieties (A) have undergone a marked downfield shift relative to those of the free ligand\* while the resonances of the B sites reveal only a very small downfield shift (H-3) or even an upfield shift (H-4, H-5, 5-CH<sub>3</sub>).

The two imine-H resonances of the copper(I) complexes appear as singlets whereas in the case of the silver(I) complexes these resonances were split due to  $^3J(^1H-^{107,109}Ag)$ .

On increasing the temperature above 220 K the  $^1H$  NMR spectra (250 MHz) of the silver(I) complexes show broadening of the resonances and loss of the  $^3J(^1H-^{107,109}Ag)$ . At 294 K only one thiophene-imine pattern is observed in which the imine-H resonance appeared as one singlet. These results indicate that in solutions of the  $[Ag_2(1)_2]^{2+}$  dications there is not only an intermolecular  $Ag^+$  (or ligand) exchange taking place above 220 K (loss of  $^3J(^1H-^{107,109}Ag)$ ), but also that a fast H(A),-H(B) exchange process is occurring (one 5-R-thiophene-imine  $^1H$  pattern at 294 K). Only one thiophene-imine  $^1H$  pattern was also observed for the  $[Cu_2(1a)_2]^{2+}$  dication (5-R = H) at 294 K. It can be concluded therefore that in this dication H(A),-H(B) exchange is likewise fast at 294 K. However, because of the lack of  $^3J(^1H-^{63,65}Cu)$  it is not possible to determine whether intermolecular ( $Cu^+$  or ligand) exchange processes are taking place in solutions of  $[Cu_2(1a)_2]^{2+}$ .

The  $^1H$  NMR spectrum (250 MHz) of  $[Cu_2(1b)_2](O_3SCF_3)_2$  showed at 294 K two separate 5-Me-thiophene-2-CH=N  $^1H$  patterns indicating that the dication of this complex has a rigid structure in solution to 294 K.

\*The dynamic behaviour of the free  $N_2S_2$  ligands **1a** and **1b** has been discussed in a previous paper [5].

In order to investigate whether there are metal IB-sulfur interactions in the  $[M_2(N_2S_2)_2]^{2+}$  dications in solution, reactions of  $[Ag(O_3SCF_3)]$  with the  $N_2$  donor ligand system (R)(S)-1,2-(3-Me-benzene-CH=N)<sub>2</sub>-cyclohexane (**2**) (see Fig. 4) were performed. Furthermore,  $^{109}Ag$  NMR spectra have been recorded of the  $[Ag_2(1)_2]^{2+}$  dications to study whether the change in 5-R-substituents (R = H or Me) has any influence on the  $\delta^{109}Ag$  value. These data provide indirect information concerning the Ag(I)-S interactions (*vide infra*).

The presence of a  $^3J(^1H-^{107,109}Ag)$  in the  $^1H$  NMR spectra of  $[Ag_2(1)_2](O_3SCF_3)_2$  at 190 K in  $CD_2Cl_2$  made it possible to record  $^{109}Ag$  NMR spectra *via* the INEPT sequence [2]. The  $^{109}Ag$  chemical shift value (relative to 2M  $AgNO_3$  in  $D_2O$ ) of  $[Ag_2(1a)_2]^{2+}$  (R = H) is  $\delta + 678$  and of  $[Ag_2(1b)_2]^{2+}$  (R = Me)  $\delta + 659^{**}$ . Thus when changing the 5-R-substituent from H to Me an upfield shift of 19 ppm is observed. This  $\Delta\delta^{109}Ag$  value may be caused by a difference in Ag-S interactions resulting from a different donor strength of the thiophene-S donor atom caused by the ortho substituents, R = H or Me, present.

The  $N_2$  ligand system **2** (see Fig. 4) only contains two imine-N atoms on the 'inner' side of the system and no heteroatoms in the aromatic rings on the 'outer' sides. Reactions of **2** with  $[Ag(O_3SCF_3)]$  have been carried out in various metal salt-to-ligand ratios. A stable complex was formed when a ratio of 1/2 was used (see Experimental). This complex has a mononuclear  $[Ag(2)_2]^+(O_3SCF_3)^-$  structure with a 1/2  $Ag/N_2$  stoichiometry as confirmed by infrared spectroscopy (non-coordinating  $O_3SCF_3^-$  anions, see Table I) field-desorption mass spectrometry (see Table II) and micro-analyses.

The  $^1H$  NMR spectrum of  $[Ag(2)_2]^+$  at 190 K in  $CD_2Cl_2$  showed two separate imine-H resonances, which were doublets due to  $^3J(^1H-^{107,109}Ag)$  [ $\delta = 8.70$ ,  $^3J = 12.3$  Hz;  $\delta = 8.38$ ,  $^3J = 6.3$  Hz]. These results indicate that the silver(I) centre is coordinated strongly by one imine-N site of each  $N_2$  ligand and that there are two weaker interactions between the metal centre with the other imine-N atom of the ligands. The complex has most probably a molecular geometry similar to that found for the  $[Ag(1b)_2]^+$  cation [5].

Attempts to obtain a dinuclear complex, having a  $[Ag_2(N_2)_2](O_3SCF_3)_2$  structure, failed. The  $^1H$  NMR spectrum at 190 K in  $CD_2Cl_2$  of a mixture of the  $N_2$  ligand **2** and  $[Ag(O_3SCF_3)]$  in a 1/1 ratio showed two singlet imine-H resonances, which have chemical shifts identical to those of the doublet imine-H resonances of  $[Ag(2)_2]^+$ . The chemical shift data and the lack of  $^3J(^1H-^{107,109}Ag)$  on the

\*\*A positive  $\delta$  corresponds to a higher resonance frequency ('deshielding') with respect to the reference frequency.

SITE

A H(im)

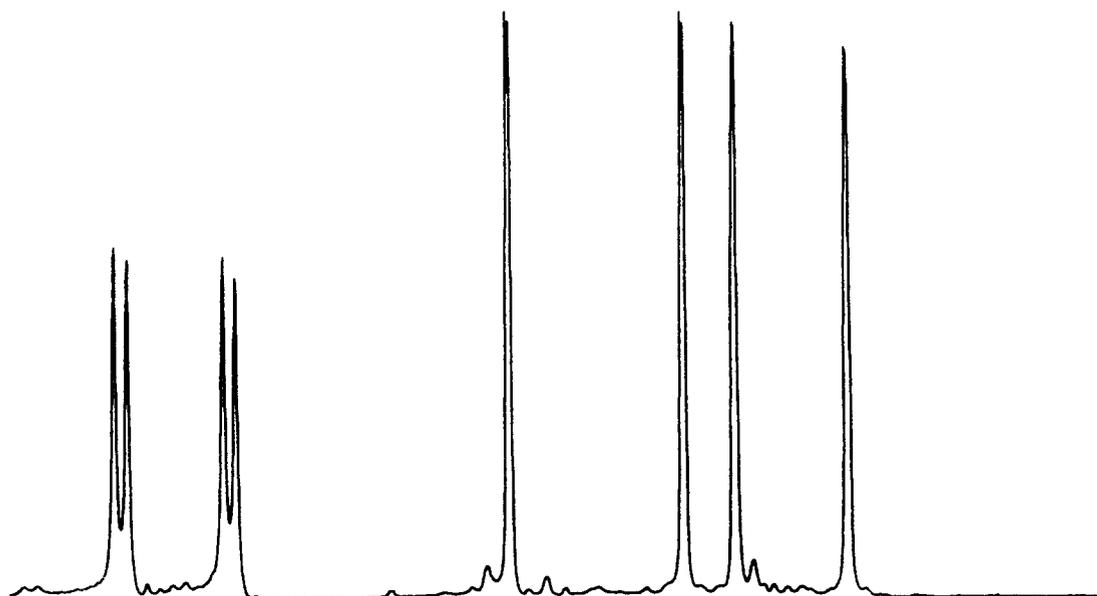
H-3

H-4

B H(im)

H-3

H-4



SITE

A H(im)

H-3

H-4

B H(im)

H-3

H-4

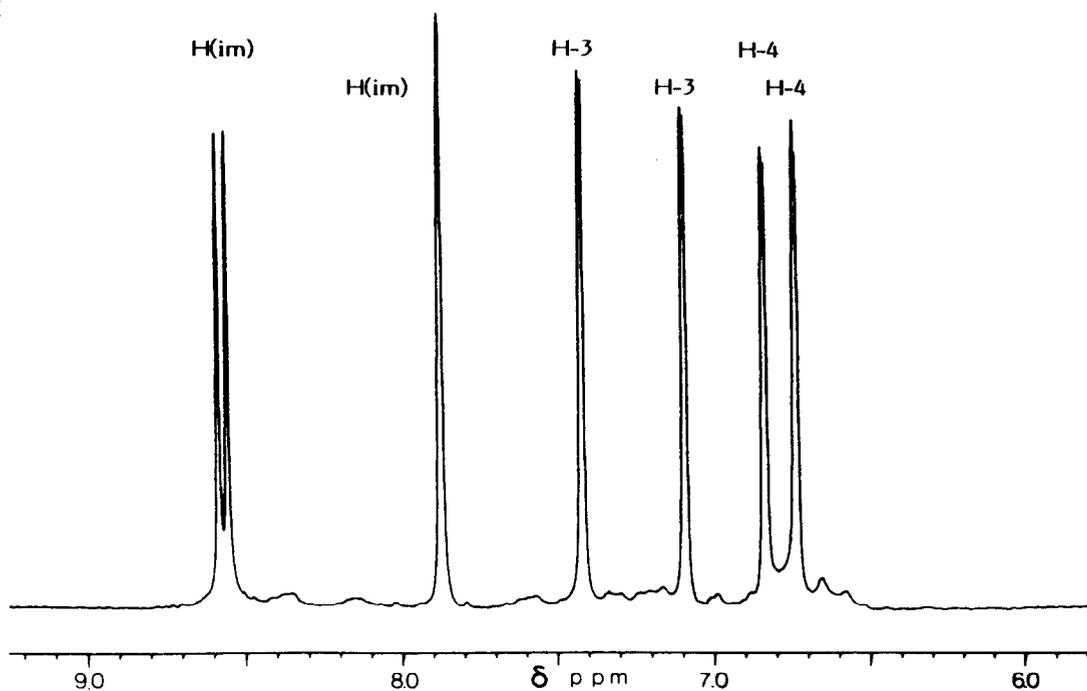


Fig. 3. The aromatic region of the  $^1\text{H}$  NMR (400 MHz,  $T = 190$  K) spectra in  $\text{CD}_2\text{Cl}_2$  of the silver(I) complexes  $[\text{Ag}_2(\text{1b})_2](\text{O}_3\text{SCF}_3)_2$  (top) and  $[\text{Ag}(\text{1b})_2](\text{O}_3\text{SCF}_3)$  (bottom).

imine-H resonances strongly suggest that in this 1/1 mixture one actually has an equilibrium between  $[\text{Ag}_2]_2(\text{O}_3\text{SCF}_3)$  and free  $[\text{Ag}(\text{O}_3\text{SCF}_3)]$  which is in the fast exchange.

From these results it may be concluded that the  $[\text{M}_2(\text{N}_2\text{S}_2)_2]^{2+}$  structures are stabilized by the presence of thiophene-S atoms and therefore M-S interactions must be present in these dications.

TABLE IV.  $^1H$  NMR Data<sup>a</sup> of the  $N_2S_2$ , **1a** and **1b**, the  $N_2$  Ligand, **2** and the Silver(I) and Copper(I) Complexes.

Compound		$\delta$ (ppm) [ $J$ (Hz)] <sup>b</sup>					
		H(im)	H-3	H-4	H-5	H(5-Me)	$\alpha$ -H
Ligands	Site						
<b>1a</b>		8.35s	7.38d	7.04b	7.27d		3.45m
		8.18s	7.33d		7.23d		
<b>1b</b>		8.22s	7.03d	6.70d		2.45s	3.35m
		8.07s				2.39s	
<b>2</b>		8.22s				2.52s	3.52m
Complexes							
$[Ag_2(1a)_2]^{2+}$	A	9.10d [16.8]	7.60d	7.27dd	7.89d		4.42m
	B	8.61d [16.1]	7.37d	6.83dd	7.09d		4.29m
$[Ag_2(1b)_2]^{2+}$	A	8.90d [16.4]	7.68d	6.96d		2.48s	4.29m
	B	8.57d [15.8]	7.13d	6.60d		2.34s	4.15m
$[Cu_2(1a)_2]^{2+}$	A	9.07s	7.63d	7.23dd	7.95d		
	B	8.54s	7.55d	6.85dd	7.00d		
$[Cu_2(1b)_2]^{2+ c}$	A	9.03s	7.79d	6.96d		2.51s	4.57m
	B	8.53s	7.06d	6.69d		2.49s	4.26m
Cu-CO (R = H)		8.63b	7.69b	7.17b	7.65b		
Cu-CO (R = Me)	A	8.47s	7.50d	6.90d		2.56s	3.91m
	B		7.42d	6.82d			3.71m
$[Ag(2)_2]^+$	A	8.70d [12.3]				2.38s	3.55m
	B	8.38d [6.3]				2.13s	

<sup>a</sup> Spectra were taken in  $CD_2Cl_2$  at  $T = 190$  K unless otherwise noted. <sup>b</sup> $^3J(^1H-^{107,109}Ag)$ . <sup>c</sup>Spectrum taken at 294 K; s = singlet, d = doublet, dd = doublet of doublets, se = septet, m = multiplet, b = broad.

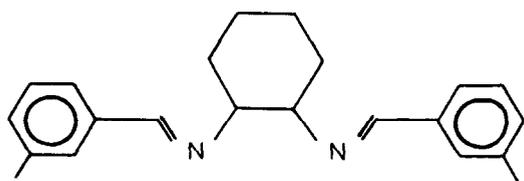


Fig. 4. Schematic representation of the  $N_2$  ligand  $(R)(S)-1,2-(3-Me-benzene-CH=N)_2-cyclohexane$ .

#### Reactions of $[M_2(1)_2](O_3SCF_3)_2$ with CO

Copper(I) centres in biological systems like hemo-cyanin have an affinity for small molecules such as  $O_2$  and CO [15]. In Cu(I) coordination complexes such an affinity is usually not found because copper(I), which is a  $d^{10}$  metal, has a low capability for  $\pi$ -backbonding [16]. Therefore, it is important to investigate in model systems under what circumstances these small molecules do coordinate to copper(I). For this reason reactions have been carried out between the  $[M_2(1)_2](O_3SCF_3)_2$  complexes [ $M = Ag(I)$  or  $Cu(I)$ ] and CO.

The silver(I) complexes,  $[Ag_2(1)_2](O_3SCF_3)_2$ , did not show any affinity for coordination of CO

in  $CH_2Cl_2$  under 1.5 bar pressure. But when the copper(I) complexes were kept under this CO atmosphere in  $CH_2Cl_2$  for a few seconds the yellow solutions became colourless. The IR spectra of samples of these solutions showed one sharp band at  $2089\text{ cm}^{-1}$  for the complex obtained from the reaction of  $[Cu_2(1a)_2](O_3SCF_3)_2$  with CO and at  $2087\text{ cm}^{-1}$  for the one formed in the reaction of  $[Cu_2(1b)_2](O_3SCF_3)_2$  with CO. The reactions are fully reversible, *i.e.*, when the solutions in  $CH_2Cl_2$  of the Cu-CO complexes were set under reduced pressure (0.1 mmHg) on a vacuum pump for one minute and then under a nitrogen atmosphere the  $[Cu_2(1)_2](O_3SCF_3)_2$  complexes were reformed. The CO complexes could be obtained in high yields as white solids only when workup proceeded in a CO atmosphere (see Experimental). Infrared spectra of the solid complexes showed one sharp signal at  $2089\text{ cm}^{-1}$  when  $5-R = H$  and at  $2091\text{ cm}^{-1}$  when  $5-R = Me$ . The IR data of the CO complexes in solution as well as in the solid indicate that the CO groups are terminally coordinated to copper(I) centres. Values of  $\nu(CO)$  of about  $2090\text{ cm}^{-1}$  are normally found for this type of CO coordination [16, 17].

The IR spectra of the solid complexes furthermore show an extra band indicating that the triflate groups also coordinate to the copper(I) centres. The broad band at  $1270\text{ cm}^{-1}$  (5-R = H) and  $1263\text{ cm}^{-1}$  (5-R = Me) for  $[\text{Cu}_2(\mathbf{1})_2](\text{O}_3\text{SCF}_3)_2$  is split in the spectra of the Cu-CO complexes into two bands at  $1296\text{ cm}^{-1}$ ,  $1240\text{ cm}^{-1}$  (5-R = H) and  $1293\text{ cm}^{-1}$ ,  $1240\text{ cm}^{-1}$  (5-R = Me). These splittings are due to a lowering in symmetry of the  $\text{O}_3\text{SCF}_3^-$  anions in the  $[\text{Cu}_2(\mathbf{1})_2](\text{O}_3\text{SCF}_3)_2$  complexes from  $C_{3v}$  to  $C_s$  which points to monodentate coordination of the  $\text{OSO}_2\text{CF}_3$  groups in the Cu-CO complexes [18].

On the basis of these results it was concluded that the CO complexes have a dinuclear neutral  $[\{\text{CuCO}(\text{OSO}_2\text{CF}_3)\}_2\{\mu\text{-N}_2\text{S}_2\}_2]$  type of structure (see Fig. 5). However, it was not possible to establish with certainty the dimeric nature of these complexes with F.D.-mass spectrometry because of CO loss under reduced pressure. The F.D.-mass spectra of the Cu-CO complexes showed patterns which were identical to those found for the dimeric  $[\text{Cu}_2(\mathbf{1})_2](\text{O}_3\text{SCF}_3)_2$  complexes.

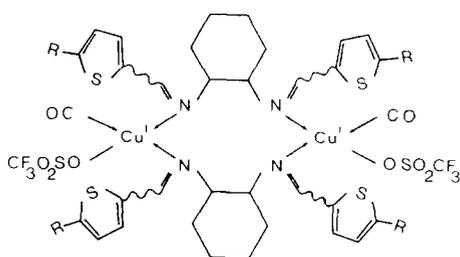


Fig. 5. Schematic representation of the Cu-CO complexes  $[\{\text{CuCO}(\text{OSO}_2\text{CF}_3)\}_2\{\mu\text{-N}_2\text{S}_2\}_2]$ .

#### The Cu-CO Complexes in Solution

Fluorine-19 NMR spectra of the Cu-CO complexes in  $\text{CD}_2\text{Cl}_2$  at 190 K (see Experimental) contain one broad signal at  $\delta -77.6^*$  for each complex. These chemical shifts are 1 ppm downfield of those found for the  $\text{O}_3\text{SCF}_3^-$  anions of the  $[\text{Cu}_2(\mathbf{1})_2](\text{O}_3\text{SCF}_3)_2$  complexes, indicating that also in solution an interaction is present between the copper(I) centres and the  $\text{OSO}_2\text{CF}_3$  groups of the Cu-CO complexes.

The  $^1\text{H}$  NMR spectrum of the Cu-CO complex containing the ligands **1a** (5-R = H) shows at 190 K (the lower temperature limit) in  $\text{CD}_2\text{Cl}_2$  only one thiophene-imine  $^1\text{H}$  pattern. The resonances at this temperature are slightly broadened. The spectrum of the Cu-CO complex containing **1b** shows at

190 K one broad singlet  $^1\text{H}$  resonance for the imine-H and 5-Me atoms but two resonances with small chemical shift differences (see Table IV) for the thiophene-H-3, H-4 and cyclohexanediyl  $\alpha$ -H atoms. At 294 K for both  $[\{\text{CuCO}(\text{OSO}_2\text{CF}_3)\}_2(\mathbf{1})_2]$  complexes there is observed one 5-R-thiophene-2-CH=N- $^1\text{H}$  pattern having sharp signals.

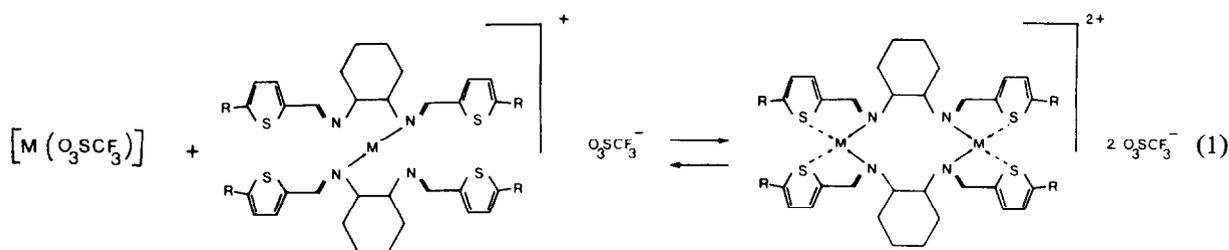
From the considerable  $^1\text{H}$  chemical shift differences between the resonances of the Cu-CO complexes and those of the free  $\text{N}_2\text{S}_2$  ligands it can be concluded that the  $\text{N}_2\text{S}_2$  ligands do coordinate to the copper(I) centres. The observation of only one thiophene-imine  $^1\text{H}$  pattern for  $[\{\text{CuCO}(\text{OSO}_2\text{CF}_3)\}_2(\mathbf{1b})_2]$  at 294 K whereas for  $[\text{Cu}_2(\mathbf{1b})_2]^{2+}$  two such patterns are observed and the fact that the CO and  $\text{OSO}_2\text{CF}_3$  groups coordinate to the copper(I) centres suggest that the  $\text{N}_2\text{S}_2$  ligands are only bonded to the metal IB centres *via* the imine-N atoms.

#### Discussion

The two different complexes; *i.e.* mononuclear  $[\text{M}(\text{N}_2\text{S}_2)_2](\text{O}_3\text{SCF}_3)$  and dinuclear  $[\text{M}_2(\text{N}_2\text{S}_2)_2](\text{O}_3\text{SCF}_3)_2$ , which are formed in the respective 2/1 and 1/1 reactions of the  $\text{N}_2\text{S}_2$  ligand system (*R*)(*S*)-1,2-(5-R-thiophene-2-CH=N)<sub>2</sub>-cyclohexane (R = H, **1a** or Me, **1b**) with  $[\text{M}(\text{O}_3\text{SCF}_3)]$  [M = Ag(I) or Cu(I)], could be isolated in the pure state and solutions of the pure complexes in  $\text{CH}_2\text{Cl}_2$  are stable. In their  $^1\text{H}$  NMR spectra only the resonance pattern of the dissolved complex is visible. Yet the  $^1\text{H}$  NMR spectra of a solution containing a mixture of the two different species [M = Ag(I), 5-R = Me] established that these complexes are in equilibrium with each other (see eqn. 1). This intermolecular exchange process is in the slow exchange limit at 190 K.

It has been shown from X-ray structure determinations that in the solid the metal IB centre in the mononuclear  $[\text{M}(\text{N}_2\text{S}_2)_2]^+$  cation [M = Ag(I) or Cu(I)] has a geometry that lies between those expected for ideal linear and tetrahedral coordination [5]. INEPT  $^{15}\text{N}$  and  $^{109}\text{Ag}$  NMR studies of  $[\text{Ag}(\mathbf{1b})_2](\text{O}_3\text{SCF}_3)$  revealed that only one imine-N site of each ligand is strongly bonded to silver(I) and that interactions between the metal IB centre and the lone pairs of the other two imine-N atoms, although very weak, do exist. Furthermore, it could be concluded that interactions in these mononuclear cations between thiophene-S atoms and the silver(I) centre are negligible [5]. It is shown that on addition of  $[\text{Ag}(\text{O}_3\text{SCF}_3)]$  to solutions of  $[\text{Ag}(\mathbf{1})_2]^+$  association of  $\text{Ag}'$  ( $\text{Ag}' = [\text{Ag}(\text{O}_3\text{SCF}_3)]$  or  $\text{Ag}^+$ ) with the weakly coordinated thiophene-imine moieties can take place. Via further Ag-N(imine) dissociation and  $\text{Ag}'$  association reactions the dinuclear  $[\text{Ag}_2(\mathbf{1})_2]^{2+}$  dication is formed.

\*A positive  $\delta$  corresponds to a higher resonance frequency ('deshielding') with respect to the reference frequency.



The molecular structure of  $[Ag_2(\mathbf{1a})_2]^{2+}$  (see Fig. 2) shows that the two  $N_2S_2$  ligands coordinate to two silver(I) centres in a bridging manner. The dication has a two fold axial symmetry in which the two cyclohexanediyl bridging groups are directed towards the metal centres and have equivalent conformations,  $\delta\delta$  or  $\lambda\lambda$ , in combination with  $\Delta\Delta$  or  $\Lambda\Lambda$  configurations of the metal IB centres. The four thiophene-imine moieties are planar as a result of their conjugated  $\pi$ -system [5]. These observations, which are directly related with the conformation of the  $N_2S_2$  ligand system, parallel those made earlier for the molecular structure of the  $[Ag_2(N_4)_2]^{2+}$  dication with the  $N_4$  donor ligand (*R*)(*S*)-1,2-(py-2-CH=N)<sub>2</sub>-cyclohexane. The  $N_4$  ligands in the latter dication adopt conformations similar to those of the  $N_2S_2$  ligands in  $[Ag_2(\mathbf{1a})_2]^{2+}$ . This conclusion is based on a comparison of the N-C-C-N torsion angles, connecting the thiophene-imine and pyridine-imine moieties in the respective complexes as well as on the fact that the thiophene-imine moieties in  $[Ag_2(\mathbf{1a})_2]^{2+}$  and the pyridine-imine moieties in  $[Ag_2(N_4)_2]^{2+}$  are both planar (see Table V).

The difference in the structures of  $[Ag_2(\mathbf{1a})_2]^{2+}$  and  $[Ag_2(N_4)_2]^{2+}$  are concerned primarily with the metal-to-ligand attachments. Each silver(I) centre in the  $[Ag_2(N_4)_2]^{2+}$  dication has a pseudo-tetrahedral geometry and possesses a short imine-N-Ag and pyridine-N-Ag bond and a long imine-N-Ag and pyridine-N-Ag interaction. The N-Ag-N angle between the two strongly bonded N sites, comprising one imine-N and one pyridine-N site is  $147^\circ$ . The N-Ag-N angles between the two imine-N sites are  $136^\circ$ . In contrast to this involvement of all four N donor sites of the  $N_4$  ligand in the metal-to-ligand bonding the  $N_2S_2$  ligands in  $[Ag_2(N_2S_2)_2]^{2+}$  are primarily bonded via the imine-N donor sites with N-Ag-N angles close to the ideal value ( $180^\circ$ ) for linear coordination. The  $^{109}\text{Ag}$  NMR data revealed that the S atoms interact weakly with the Ag atoms and it is most probably these interactions which stabilize the dinuclear cation. If these 'outer' heteroatoms are absent as in the  $N_2$  ligand 2 only the mononuclear 1/2 complex  $[Ag(2)_2](O_3SCF_3)$  could be obtained even in the presence of excess  $[Ag(O_3SCF_3)]$ . This is not surprising when one considers that in the  $[M_2(N_2S_2)_2]^{2+}$  dications the lone pairs of the

thiophene-S atoms are pointing towards the electrophilic metal IB centre while in the  $N_2$  system such electron donors in the outer ring systems (3-Me-benzene moieties) are lacking, instead only C-H groups are present.

An obvious consequence of the different coordination behaviour of the  $N_2S_2$  and  $N_4$  ligands in the respective dications is the different Ag-Ag distance in these dinuclear species. In  $[Ag_2(\mathbf{1a})_2]^{2+}$  this distance is remarkably shorter, 2.909(1) Å, than that in  $[Ag_2(N_4)_2]^{2+}$ , 3.254(2) Å. Furthermore, because of the different silver(I) geometries in the dications the molecular structure of  $[Ag_2(\mathbf{1a})_2]^{2+}$  is folded more openly, *i.e.* the distance between the (*R*)(*S*)-1,2-cyclohexanediyl groups is larger than in the  $[Ag_2(N_4)_2]^{2+}$  structure (see Fig. 6). Accordingly the metal IB centres in the  $[Ag_2(N_2S_2)_2]^{2+}$  dication are less shielded for attack by other substrates. From these observations it can be concluded therefore that in these dications, although the conformation of the ligand backbone is having some influence, it is primarily the number and nature of donor heteroatoms which determine the way the polydentate ligands coordinate to the metal IB centres.

Because of the very weak thiophene-S-Ag interactions in  $[Ag_2(\mathbf{1a})_2]^{2+}$  compared to the strong pyridine-N-Ag in  $[Ag_2(N_4)_2]^{2+}$  the silver(I) centres in  $[Ag_2(\mathbf{1a})_2]^{2+}$  are primarily coordinated by the imine-N sites. These different metal-to-ligand attachments cause the positional differences of the entire ligand systems in the two dications.

#### $[M_2(\mathbf{1})_2](O_3SCF_3)_2$ [ $M = Ag(I)$ or $Cu(I)$ ] Complexes in Solution

From the  $^{19}\text{F}$  and  $^1\text{H}$  NMR results it is concluded that the complexes obtained from the 1/1 molar reactions of the  $N_2S_2$  ligands 1 with  $[M(O_3SCF_3)]$  [ $M = Ag(I)$  or  $Cu(I)$ ] have in solution a  $[M_2(\mathbf{1})_2]^{2+} \cdot 2(O_3SCF_3)^-$  type of structure. All available data rule out a mononuclear  $[M(\mathbf{1})OSO_2CF_3]$  or a dinuclear  $[M(\mathbf{1})_2][M(O_3SCF_3)_2]^*$  formulation for these complexes.

\*When the dinuclear complexes have a  $[M(\mathbf{1})_2]^+[M(O_3SCF_3)_2]^-$  type of structure in solution  $^1\text{H}$  NMR spectra would be expected similar to those observed for the  $[M(\mathbf{1})_2]^+(O_3SCF_3)^-$  complexes [5]. This is not the case (*cf.* Fig. 3).

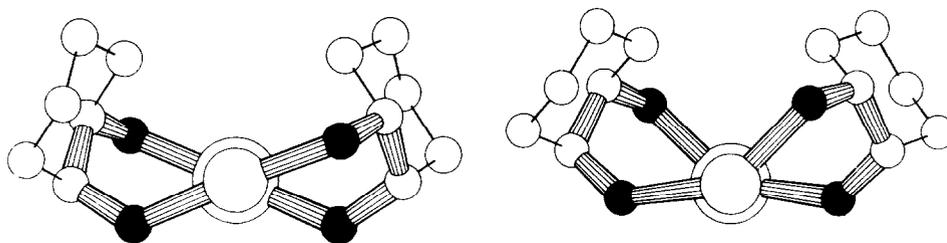


Fig. 6. Projections down the Ag–Ag axis of the *endo*- $\Delta_{SR}^{RS}$  forms of  $[\text{Ag}_2(\mathbf{1a})_2]^{2+}$  (left) and  $[\text{Ag}_2(\text{N}_4)_2]^{2+}$  (right).

TABLE V. Comparison of the Ag–N and Ag–S Bond Lengths and a Conformational Analysis of the  $\text{N}_2\text{S}_2$  and  $\text{N}_4^a$  Ligands in the Structures of  $[\text{Ag}_2(\text{N}_2\text{S}_2)_2]^{2+}$  and  $[\text{Ag}_2(\text{N}_4)_2]^{2+}$ .

$[\text{Ag}_2(\text{N}_2\text{S}_2)_2]^{2+}$			$[\text{Ag}_2(\text{N}_4)_2]^{2+}$		
Bond lengths (Å)					
S(1)–Ag(1)	2.961(4)		N(1)–Ag(1)	2.455(12)	
N(2)–Ag(1)	2.152(10)		N(2)–Ag(1)	2.251(11)	
N(3)–Ag(2)	2.153(10)		N(3)–Ag(2)	2.430(11)	
S(4)–Ag(2)	2.928(4)		N(4)–Ag(2)	2.252(13)	
S(5)–Ag(2)	2.995(5)		N(5)–Ag(2)	2.429(11)	
N(6)–Ag(2)	2.158(10)		N(6)–Ag(2)	2.240(12)	
N(7)–Ag(1)	2.162(9)		N(7)–Ag(1)	2.440(11)	
S(8)–Ag(1)	2.938(4)		N(8)–Ag(1)	2.242(11)	
Ag(1)···Ag(2)	2.909(1)		Ag(1)···Ag(2)	3.254(2)	
Torsion angles (°)					
S(1)–N(2)	–3(2)	(sp) <sup>b</sup>	N(1)–N(2)	15(2)	(sp) <sup>b</sup>
C(5)–C(7)	173(1)	(ap)	C(5)–C(7)	176(1)	(ap)
C(6)–C(12)	118(1)	(ac)	C(6)–C(12)	142(1)	(ac)
N(2)–N(3)	57(1)	(sc)	N(2)–N(3)	58(1)	(sc)
C(7)–C(13)	–144(1)	(ac)	C(7)–C(13)	–148(1)	(ac)
C(12)–C(14)	–172(1)	(ap)	C(12)–C(14)	–178(1)	(ap)
N(3)–S(4)	5(2)	(sp)	N(3)–N(4)	3(2)	(sp)
S(5)–N(6)	–10(2)	(sp)	N(5)–N(6)	4(2)	(sp)
C(23)–C(25)	175(1)	(ap)	C(23)–C(25)	177(1)	(ap)
C(24)–C(30)	110(1)	(ac)	C(24)–C(30)	136(1)	(ac)
N(6)–N(7)	55(1)	(sc)	N(6)–N(7)	59(1)	(sc)
C(25)–C(31)	–138(1)	(ac)	C(25)–C(31)	–151(1)	(ac)
C(30)–C(32)	–174(1)	(ap)	C(30)–C(32)	–174(1)	(ap)
N(7)–S(8)	8(2)	(sp)	N(7)–N(8)	0(2)	(sp)

<sup>a</sup> $\text{N}_4 = (R)(S)$ -1,2-(py-2-CH=N)<sub>2</sub>-cyclohexane [2]. <sup>b</sup>For the abbreviations of sp = synperiplanar, ap = antiperiplanar, ac = anticlinal and sc = synclinal, see ref. 23.

The  $[\text{M}_2(\mathbf{1})_2]^{2+}$  dications can exist in different stereoisomeric forms in solution at 190 K. The observation of only one <sup>109</sup>Ag resonance in the <sup>109</sup>Ag NMR spectra of  $[\text{Ag}_2(\mathbf{1})_2]^{2+}$  (at 190 K) reveals that these stereoisomers must possess a two-fold axial symmetry. One of the possible structures is illustrated in the PLUTO drawing of  $[\text{Ag}_2(\mathbf{1a})_2]^{2+}$  in Fig. 2. In this structure both silver(I) centres have the  $\Delta$  configuration and the (R)(S)-cyclohexanediyl bridges are pointing towards each other (*endo*). This structure can be denoted as *endo*- $\Delta_{SR}^{RS}$  [4].

In the case of the  $[\text{Ag}_2(\text{N}_4)_2]^{2+}$  dications the <sup>1</sup>H, <sup>15</sup>N and <sup>109</sup>Ag NMR<sup>†</sup> results indicated that

these dications only exist in solution in the *endo*- $\Delta_{SR}^{RS}$  form [4]. When this is also true for the  $[\text{M}_2(\text{N}_2\text{S}_2)_2]^{2+}$  dications a rationale can be given for the very different chemical shifts of the two thiophene-imine patterns (at 190 K). The PLUTO drawing in Fig. 2 of  $[\text{Ag}_2(\mathbf{1a})_2]^{2+}$  shows that in contrast to the well separated thiophene rings (A) the other two thiophene rings (B) are parallel positioned. The H-atoms of the latter rings therefore experience a ring current effect. The upfield

<sup>†</sup>For  $[\text{Ag}_2(\text{N}_4)_2](\text{O}_3\text{SCF}_3)_2$   $\delta^{109}\text{Ag} = +580$  when 6-R = H and +612 when 6-R = Me. These data were obtained in methanol-d<sub>4</sub> at 294 K. The  $\Delta\delta/\text{K}$  value for the complex with 6-R = Me is –0.25 ppm/K.

shifts of the  $^1H$  resonances of site B of the  $[M_2\text{-}(1)_2]^{2+}$  dications (see Table IV), relative to the corresponding resonances of site A, can then be ascribed as arising from this ring current. As pointed out in the Results section the silver(I) complexes are prone to intermolecular exchange processes above 220 K (as evidenced by the loss of the  $^3J(^1H\text{-}^{107,109}Ag)$  on the imine-H resonances) and these cause the separate thiophene-imine  $^1H$  patterns, A and B, to coalesce to one pattern such as observed in the  $^1H$  NMR spectra at 294 K.

For the copper(I) complexes  $[Cu_2(1)_2](O_3SCF_3)_2$  it was not possible to determine with certainty whether intermolecular exchange processes are taking place in solution of these complexes because  $^3J(^1H\text{-}^{63,65}Cu)$  are not resolved.

The observed H(A),-H(B) exchange process above 220 K in solutions of  $[Cu_2(1a)_2]^{2+}$  can be caused by an intermolecular ( $Cu^+$  or ligand) exchange as well as by an intramolecular process. A study on molecular models showed that the intramolecular process comprises Cu-S (thiophene) bond rupture at both ends of the dication after which inversion of configuration at the metal IB centres may take place ( $\Delta\Delta\text{-}\Delta\Delta$ ). When this inversion takes place it is observed as H(A),-H(B) exchange in the  $^1H$  NMR spectra.

However, the fact that the copper(I) complex  $[Cu_2(1b)_2](O_3SCF_3)_2$  produces two thiophene-imine  $^1H$  patterns even at 294 K, *i.e.* the H(A),-H(B) exchange is still in the slow exchange limit, is an indication that, i) the thiophene-S atoms have stronger interactions with the copper(I) centres in  $[Cu_2(1b)_2]^{2+}$  than those in the corresponding silver(I) dication and ii) the H(A),-H(B) exchange, observed in solutions of  $[Cu_2(1a)_2]^{2+}$  is caused by an intermolecular process. Apparently, the 5-R substituents have a great influence on the rate of the exchange process. Such an influence has been observed before for the intermolecular exchange processes occurring in solutions of the  $[Ag_2(N_4)_2]^{2+}$  dications ( $N_4 = (6\text{-}R\text{-}py\text{-}2\text{-}CH=N)_2\text{-}R'$ ,  $R' = (R)\text{-}(S)\text{-}1,2\text{-}cyclohexane$  or  $1,2\text{-}ethane$ ,  $R = H$  or  $Me$ ) [4]. When the substituent R was H in the latter dications intermolecular  $Ag^+$  or  $N_4$  ligand exchange proceeded much faster than when R was the bulkier Me group. This was ascribed to the shielding effect of the Me group making it difficult for  $Ag^+$  or free  $N_4$  ligand to attack a pyridine-N site or a  $Ag^+$  centre respectively of the  $[Ag_2(N_4)_2]^{2+}$  dication [4]. In the  $[Cu_2(1b)_2]^{2+}$  dication the presence of a 5-Me substituent obviously exhibits a similar shielding effect thus making it less likely for an intermolecular  $Cu^+$  or free  $N_2S_2$  ligand exchange to proceed.

#### Copper-CO Complexes

The fixation of CO by copper(I) is of interest and importance both in the area of metal promoted

CO reduction [19] and in the simulation of naturally occurring systems containing copper(I) [20]. For instance the reaction of deoxy-hemocyanin with carbon monoxide yielded a product in which only one molecule of CO is coordinated terminally ( $\nu(CO) = 2063\text{ cm}^{-1}$ ) to one of the two copper(I) centres [15].

In order to determine the prerequisite for copper(I) centres to bind CO various research groups have synthesized and characterized Cu-CO coordination complexes [17]. These complexes contain polydentate ligand systems, which are coordinated to one or more metal centres in a similar way both before and after the reaction with CO. Frequent use has been made of for instance (bis)-tridentate ligand systems which coordinate to the copper(I) centre(s) with three heteroatoms leaving a fourth coordination place empty for CO. However, to our knowledge, it has not been reported before that CO displaces a heteroatom of a polydentate ligand system in order to bind to the copper(I) centre itself. In this study it is shown that such a replacement is possible. Weak thiophene-S-Cu interactions can be broken to establish the binding of CO with the copper(I) centres. The reversibility of the reactions of CO with  $[Cu_2(1)_2](O_3SCF_3)_2$  indicates that the Cu-CO bonds are not particularly strong. Furthermore the CO-stretching vibrations in the infrared spectra in the region of  $2090\text{ cm}^{-1}$  suggest that there is little  $\pi$ -backbonding between Cu(I) [16] and CO.

Only the Cu-CO complexes  $\{[CuCO(OSO_2CF_3)]_2\{\mu\text{-}N_2S_2\}_2\}$  having one CO group coordinating to each Cu(I) centre could be isolated. It is therefore surprising that in our Cu-CO complexes all thiophene-S-Cu interactions are broken. Apparently, it is less favourable for the  $N_2S_2$  ligands in the Cu-CO complexes to coordinate to the metal centre with two imine-N atoms and one thiophene-S atom. It is thought that the coordination behaviour of the  $N_2S_2$  ligands as observed (*i.e.* coordinating to the copper(I) centres only by the imine-N atoms) is caused by an intrinsic conformational preference of the ligand system, leaving now next to CO one coordination place for the  $OSO_2CF_3$  group to bind each Cu(I) centre. Neither complexes with two CO molecules per metal centre nor  $\{[Cu(OSO_2CF_3)\text{-}N_2S_2]_2\{\mu\text{-}CO\}\}$  complexes, containing a bridging CO group as reported by Floriani *et al.* [21] and at a later date Doyle *et al.* [22] were observed.

From the difference in reactivity of  $[Cu_2(N_2S_2)_2](O_3SCF_3)_2$  and  $[Cu_2(N_4)_2](O_3SCF_3)_2$  [2-4] towards both CO and the free ligand it can be concluded that Cu-CO complexes can only be prepared from these complexes when heteroatoms are present which have only weak interactions with the pseudo tetrahedral four coordinate metal centres and are therefore easily replaceable by other coor-

dinating agents when present. Furthermore, the copper(I) centres must be accessible to allow the carbon monoxide molecules to coordinate. This is based on the observation that despite the fact that the copper(I) centres in the  $[\text{Cu}(\text{N}_2\text{S}_2)_2]^+$  cations maintain two strong imine-N interactions and two weak imine-N interactions [5] they do not react with CO to give Cu-CO complexes. In these cations the metal IB centre is surrounded by two bulky  $\text{N}_2\text{S}_2$  ligands which make it very difficult for CO to approach the metal centre.

## Conclusions

From the 1/1 molar reactions of the  $\text{N}_2\text{S}_2$  ligand system (R)(S)-1,2-(5-(R-thiophen-2-CH=N)<sub>2</sub>-cyclohexane (R = H, **1a** or Me, **1b**) with  $[\text{M}(\text{O}_3\text{SCF}_3)]$  [M = Ag(I) or Cu(I)] the  $[\text{M}_2(\mathbf{1})_2](\text{O}_3\text{SCF}_3)_2$  complexes were obtained. These complexes have in solution at 190 K, as indicated by  $^1\text{H}$  and  $^{109}\text{Ag}$  NMR data, similar structures to that found in the solid by X-ray diffraction for  $[\text{Ag}_2(\mathbf{1a})_2](\text{O}_3\text{SCF}_3)_2$ . It is shown by the  $^1\text{H}$  and  $^{109}\text{Ag}$  NMR data that the formation of the  $[\text{M}_2(\mathbf{1})_2]^{2+}$  dications is stabilized by the presence of strong imine-N-M bonds as well as by weak thiophene-S-M interactions. The fact that the latter interactions are weak was concluded from the observation that the  $[\text{Ag}_2(\mathbf{1})_2]^{2+}$  and  $[\text{Cu}_2(\mathbf{1a})_2]^{2+}$  dications undergo intermolecular exchange processes above 220 K. Furthermore, the reactions of the  $[\text{Cu}_2(\mathbf{1})_2](\text{O}_3\text{SCF}_3)_2$  complexes with carbon monoxide yielded complexes in which the thiophene-S-Cu bonds were dissociated. In the vacant sites left one CO group and one  $\text{OSO}_2\text{CF}_3$  group coordinate to each metal IB centre yielding neutral  $\{[\text{CuCO}(\text{OSO}_2\text{CF}_3)]_2\}_{\mu-1}$  complexes. Such replacement of weakly coordinated donor sites by carbon monoxide in Cu(I) species has to our knowledge not been reported before. This reaction process may be of significance for future studies of structural and bonding features of Cu-CO complexes, not only in organo-metallic chemistry, but also in the field of biological copper containing macromolecules.

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