Synthesis, Solid-state and Solution Structures of Bis{*N,N'*-bis[(2-thienyl)methylene]-1,2-diaminoethane}-silver(I) and -copper(I) Trifluoromethanesulfonate Complexes‡

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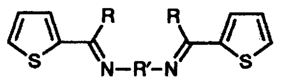
Reaction of 2 equivalents of the thienyl ketimines $[(SC_4H_3)CR{=}N]_2C_2H_4$ (R = Me or SC_4H_3) with 1 equivalent of $M^I(O_3SCF_3)$ (M = Ag or Cu) resulted in formation of stable $[M\{[(SC_4H_3)CR{=}N]_2C_2H_4\}_2][O_3SCF_3]$ complexes. The crystal structures of $[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2][O_3SCF_3]$ and $[Cu\{[(SC_4H_3)C{=}N]_2C_2H_4\}_2][O_3SCF_3]$ have been determined. Both unit cells contain discrete anions and, basically isostructural, complex cations. The co-ordination sphere of the metal(I) centre is dominated by four imine N atoms [Ag, 2.329(3); Cu, 2.014(14)–2.110(13) Å] provided by two symmetrically, bidentate co-ordinating $[(SC_4H_3)CR{=}N]_2C_2H_4$ ligands. Four thiophene S atoms are also in proximity of the metal nucleus [Ag, 3.259(2); Cu, 3.160(8)–3.438(6) Å], but do not co-ordinate. The AgN_4 geometry is flattened, as indicated by the spatial geometry of the four donor atoms, and tends more to square planar than to the usual tetrahedral arrangement. The CuN_4 geometry is slightly compressed from tetrahedral. A characteristic of these complexes is their very low solubility which makes futher spectroscopic studies difficult. Various ^1H NMR experiments have established that the complex cations are isostructural, having a tetrahedral co-ordination geometry similar to that found in the crystals, comprising symmetrically co-ordinating, bidentate ligands. There are no indications that the solution structure is compressed. The solution structure is only kinetically stable at low temperatures ($\leqslant$180 K); at more elevated temperatures ligand exchange occurs, which is rapid at ambient temperatures.

In previous papers we have reported on the synthesis and characterization of silver(I) and copper(I) complexes with the neutral N_2S_2 donor *N,N'*-bis(thienylmethyl)-1,2-(*R*),(*S*)-diaminocyclohexane.[1] As evidenced by solid-state structures, N_2S_2 compounds of this type and trifluoromethanesulfonate (triflate) metal salts $M^I(O_3SCF_3)$[2] afford either (*i*) co-ordination complexes with a metal-to-ligand stoichiometry M:L = 2:2, in which each metal(I) centre is bonded to two imine N atoms while two thiophene S atoms are in its proximity,[1a] or (*ii*) M:L = 1:2 complexes with a metal(I) cation bonded to two imine N atoms, with the two remaining imine N atoms and two thiophene S atoms in its proximity.[1b,c] Using various NMR measurements (^1H, ^{19}F, ^{109}Ag) it has been shown that the basic structure of these complexes is retained in solution, although site- and ligand-exchange processes may occur.

In view of the relative closeness of the (ald)imine H atom to both the thiophene H^3 and the α-amino function in these (ald)imine-based ligands, the substitution of the former by a more bulky group might result in some interesting changes. Therefore, we embarked on a study concerning the co-ordination behaviour of the corresponding ketimine-based N_2S_2 compounds towards silver(I) and copper(I) cations. For several reasons, this appeared to be more difficult than anticipated. First, synthetic problems were encountered in the ketimine preparation phase. Secondly, the co-ordination complexes invariably turned out to have a very low solubility, and this has frustrated in many cases the study of their solution structure. Therefore, this study has been restricted to $[(SC_4H_3)CR{=}N]_2C_2H_4$ with R = Me or SC_4H_3. We present the solid-state and solution structures of silver(I) and copper(I) complexes of these compounds having M:L = 1:2 stoichiometry, and aspects of the synthesis of the N_2S_2 compounds will also be discussed.



R = H; R' = C_6H_{10}: ref 1
R = Me or SC_4H_3; R' = C_2H_4: this work

Results and Discussion

Preparation of the Compounds.—Whereas N_2S_2 compounds of the type $[(SC_4H_3)CH{=}N]_2C_2H_4$, *i.e.* derived from thiophenecarbaldehyde, are easily accessible from a smoothly proceeding reaction,[2] corresponding ketimine-based Schiff bases are not. Condensation of a thienyl ketone and diaminoethane can only be achieved at elevated reaction temperatures using a Lewis-acid catalyst and with removal of

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† For correspondence regarding the crystallography.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

water formed. In this way we obtained pure $[(SC_4H_3)CR{=}N]_2C_2H_4$ compounds with R = Me, Et or SC_4H_3. However, with R = Pr^i or Bu^t the condensation reaction yielded a mixture, not a single product. An analysis of structural characteristics of these compounds provides an explanation for this result.

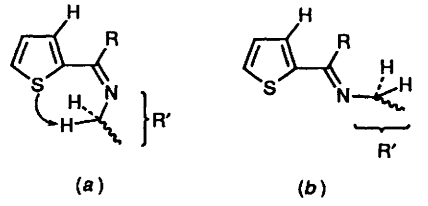
Minimum neglect of differential overlap (MNDO) and Austin model (AM1) calculations show that the thienylmethyleneamino moiety strongly prefers a planar arrangement as a result of π conjugation and the sym-*cis* conformation, *i.e.* with the N and S atoms on the same side, is more stable than the sym-*trans* form.[3] The imine bond may be formed with either *E* or *Z* configuration but, since the energy barrier between the two configurations is low,[4] only the product with the lower steric hindrance is usually isolated. The sym-*cis* conformation of the thiopheneimine backbone will disfavour a *Z* configuration at the imine bond, due to the accompanying close contact of the sulfur atom and the C_α substituents of the amino function R′ (Scheme 1). Indeed, as established by crystal structures, the $(SC_4H_3)CR{=}NR'$ unit exclusively possesses a sym-*cis* S=C–C=N conformation and an *E* C=N configuration when R = H.[5] In the corresponding ketimine moiety, where R ≠ H, this stereochemistry will give rise to a steric interaction of R with the thiophene H^3 and the $R'C_\alpha$ substituents, which will increase with the extent of substitution of the C^2 atom of the R group's C_α atom. Corey–Pauling–Koltun (CPK) molecular model studies suggest that if R = Me or Et then rotation about the C=N bond is still unhindered and rearrangement is therefore easy, resulting in a product with a unique configuration which is most probably *E*. However, in the case of the R group possessing a tertiary or quaternary C_α atom, *e.g.* R = Pr^i or Bu^t, a large increase in the rotational barrier arises and consequently the initial configuration is retained. A similar case in which both imine configurations are stabilized and the two compounds actually separated has been documented.[6] Since the present experimental findings parallel the model studies this explanation seems very likely. Thus, if R = Pr^i or Bu^t up to three different Schiff-base products may be formed. Obviously, the condensation product with symmetric $(SC_4H_3)_2C{=}O$ will always be unique.

Since all efforts aimed at obtaining pure isomers of Pr^i- or Bu^t-substituted $[(SC_4H_3)CR{=}N]_2C_2H_4$ compounds failed (see Experimental section), the study of the co-ordination behaviour was restricted to two representatives, those having the smallest (Me) and largest R substituent (SC_4H_3).

Although all concentration ratios of the $M^I(O_3SCF_3)$ salts (M = Ag or Cu) and N_2S_2 ligands lead to the isolation of stable co-ordination complexes with M:L = 1:2 stoichiometry, the complexes discussed below were specifically synthesized from 1:2 molar reactions. The ivory-brown silver(I) complexes are neither air nor light sensitive; the dark red-brown copper(I) complexes are only moderately oxygen sensitive. The complexes of both metals are insoluble in apolar solvents and have only very limited solubilities in methanol and dichloromethane.

Solid-state Structures of $[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2][O_3SCF_3]$ *and* $[Cu\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2][O_3SCF_3]$.—X-Ray structural determinations reveal that both $[M^I(N_2S_2)_2][O_3SCF_3]$ complexes consist of discrete $[M^I(N_2S_2)_2]^+$ complex cations and non-co-ordinating O_3SCF_3 anions. The unit cell of the silver(I) species contains four enantiomeric pairs of identical $[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2]^+$ complexes, each having 222 site symmetry as a result of which only a quarter of the molecule is unique. The unit cell of the copper(I) species contains two sets of two enantiomeric pairs, *i.e.* eight complexes in total. The two crystallographically independent $[Cu\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2]^+$ cations are structurally similar with virtually identical metal co-ordination geometries. The only difference between them concerns the orientation of the thiophene rings which occupy the *Z* space relative to the C=NR fragment (see below); several thiophene moieties are disordered over two orientations. Selected distances and angles of the $[M^I(N_2S_2)_2]^+$ cations are listed in Table 1; the molecular geometry and the numbering scheme adopted for $[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2]^+$ and $[Cu\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2]^+$ (molecule 1) are shown in Figs. 1 and 2, respectively.

An analysis of the N_2S_2 ligand skeleton reveals the expected[7] thienylmethyleneamino structure in the silver(I) complex, comprising an *E* C=N configuration and a sym-*cis* S=C–C=N conformation. Although the deviation of −13.3(5)° from perfect coplanarity is more than the value of 2° found in the aforementioned $[Ag\{[(SC_4H_3)CH{=}N]_2C_6H_{10}\}_2]^+$ complex,[1b]



Scheme 1 The S=C–C=N sym-*cis* conformation with (*a*) *Z* and (*b*) *E* C=N configuration

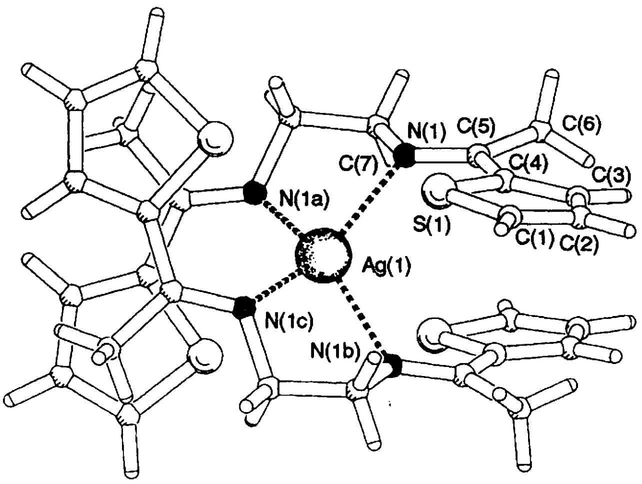


Fig. 1 A PLUTON[8] drawing of $[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2]^+$ with the atom labelling scheme

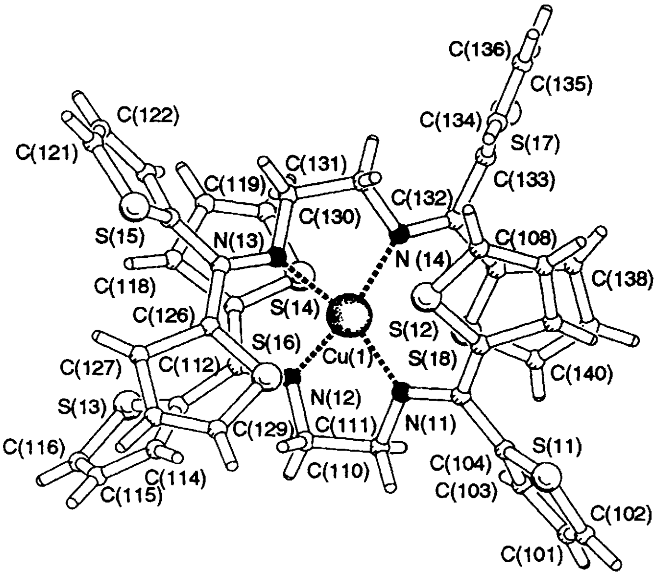


Fig. 2 A PLUTON[8] drawing of $[Cu\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2]^+$ (molecule 1) with the atom labelling scheme

Table 1 Selected distances (Å) and angles (°)

$[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2]^+$		$[Cu\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2]^+$	
Ag(1)···S(1)	3.259(2)	Cu(1)···S(11), S(13), S(15), S(17)	5.7 (average)
		Cu(1)···S(12), S(14), S(16), S(18)	3.168(6)–3.373(6)
Ag(1)–N(1)	2.329(3)	Cu(1)–N	2.014(14)–2.110(13)
S(1)–C(1)	1.693(7)	S(11)–C(101)	1.729(19)
S(1)–C(4)	1.724(5)	S(11)–C(104)	1.714(18)
N(1)–C(5)	1.282(6)	N(11)–C(105)	1.36(2)
N(1)–C(7)	1.464(5)	N(11)–C(110)	1.49(2)
C(4)–C(5)	1.457(6)	C(104)–C(105)	1.45(2)
C(5)–C(6)	1.502(7)	C(105)–C(106)	1.40(3)
C(7)–C(7a)	1.505(5)	C(110)–C(111)	1.53(2)
		C(130)–C(131)	1.53(2)
N(1)–Ag(1)–N(1a)	77.25(11)	N(11)–Cu(1)–N(12)	84.9(6)
N(1)–Ag(1)–N(1b)	112.81(11)	N(11)–Cu(1)–N(13)	139.1(6)
N(1)–Ag(1)–N(1c)	146.41(11)	N(11)–Cu(1)–N(14)	116.6(5)
N(1a)–Ag(1)–N(1b)	146.41(11)	N(12)–Cu(1)–N(13)	99.5(5)
N(1a)–Ag(1)–N(1c)	112.81(11)	N(12)–Cu(1)–N(14)	141.1(6)
N(1b)–Ag(1)–N(1c)	77.25(11)	N(13)–Cu(1)–N(14)	84.9(5)
Ag(1)–N(1)–C(5)	123.1(3)	Cu(1)–N(11)–C(105)	129.0(11)
Ag(1)–N(1)–C(7)	105.9(2)	Cu(1)–N(11)–C(110)	109.6(10)
C(5)–N(1)–C(7)	120.1(3)	C(105)–N(11)–C(110)	119.0(14)
Dihedral angles			
S(1)–C(4)–C(5)–N(1)	−13.3(5)	S(11)–C(104)–C(105)–N(11)	−139.5(15)
		S(12)–C(106)–C(105)–N(11)	32(2)

Symmetry operations: a $\frac{1}{4} - x, \frac{1}{4} - y, z$; b $x, \frac{1}{4} - y, \frac{1}{4} - z$; c $\frac{1}{4} - x, y, \frac{1}{4} - z$.

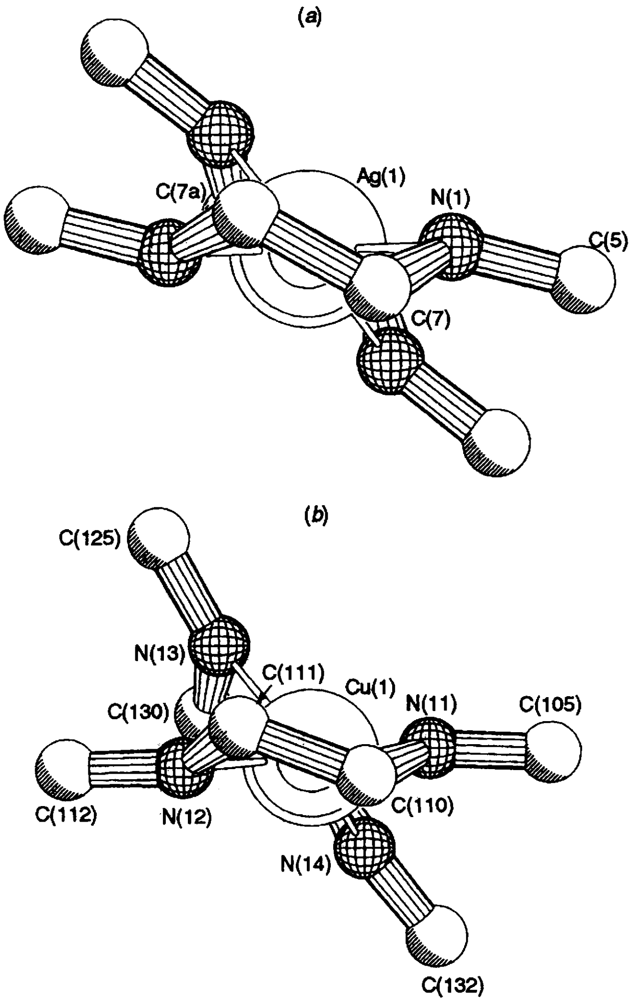


Fig. 3 Side view of the M^IN_4 co-ordination geometries

it is still less than some other reported values which are as high as 18°.[9,10]

The situation in the copper(I) species is more interesting, since from molecular model studies we know that the $(SC_4H_3)_2$-C=NR′ moiety cannot be planar. Indeed, the positioning of the eight thiophene rings relative to the C=N function is remarkable: in one of the independent molecules (1, Fig. 2) the four rings occupying the (C=NR) *E* space possess the usual sym-*cis* S=C–C=N conformation, though deviating considerably (22–34°) from perfect planarity, but the four '*Z* rings' tend to the sym-*trans* conformation (S=C–C=N, 115–150°). Most likely, this orientation represents an inherent ligand quality, *i.e.* a structural compromise independent of co-ordination, to get the maximum possible resonance stabilization. In the other molecule (2) the situation is similar with the exception that one of the four '*Z* rings' possesses the sym-*cis* conformation.

In the silver(I) complex the four thiophene '*E* rings' are, pairwise, practically parallel and within each ligand pair the methyl groups are mutually positioned *ca.* 3.4 Å above each others' ring; this is evidently intramolecular close packing. All distances and angles are well within the accepted ranges, although the C=N bond in the copper(I) complex (average 1.32 Å) is somewhat longer than the value found (average 1.27 Å) for a corresponding complex with a less bulky ligand system.[1c]

In both complexes the two N_2S_2 ligands surround the metal(I) nuclei with four imine N atoms and four thiophene S atoms. Based on literature values for the covalent radii of Cu (1.52), Ag (1.59), N (0.68) and S (1.02 Å), the long M–S distances [Ag^I, 3.259(2); Cu^I, 3.168(6)–3.373(6) Å] clearly rule out a bonding interaction, whereas the M–N distances [Ag^I, 2.329(3); Cu^I, 2.014(14)–2.110(13) Å] are well within bonding range, thus characterizing the metal co-ordination geometry as MN_4. Compared with the M^I–N distances in the $[M\{[(SC_4H_3)CH{=}N]_2C_6H_{10}\}_2]^+$ complex cations [Ag^I; 2.28(average); Cu^I, 1.92(average) Å],[1b,c] the present silver(I) value is almost identical but the corresponding copper(I) one is markedly longer, most likely attributable to the bulky $(SC_4H_3)_2C{=}N$ unit.

However, the geometry at the silver(I) centre [Fig. 3(*a*)] is rather extraordinary. First, the four donor atoms tend to a

Table 2 Proton and ^{19}F NMR data for $[(SC_4H_3)CR{=}N]_2C_2H_4$ L and $[M\{[(SC_4H_3)CR{=}N]_2C_2H_4\}_2][O_3SCF_3]$ ML_2[a]

	$[(SC_4H_3)CMe{=}N]_2C_2H_4$			$[(SC_4H_3)_2C{=}N]_2C_2H_4$		
Function	L	AgL_2	CuL_2	L	AgL_2	CuL_2
CH_2	3.82 (s)	3.46 (s)[b]	≈3.3[c]	3.80 (s)	3.63 (s)	3.52 (s)
H^4	7.02 (dd)	7.10 (dd)	7.14 (dd)	7.17 (dd)	7.17 (dd)	7.18 (dd)
				7.00 (dd)	7.08 (dd)	7.12 (dd)
H^3,H^5	7.43 (d)	7.45 (d, H^3)[d]	7.59 (d)	7.65 (d)	7.75 (d)	7.80 (d)
	7.41 (d)	7.55 (d, H^5)[d]	7.65 (d)	7.50 (d)	7.71 (d)	7.69 (d)
				7.18 (d)	7.13 (d)	7.34 (d)
				7.00 (d)	7.07 (d)	6.95 (d)
CH_3	2.30 (s)	2.04 (s)	1.92 (s)			
O_3SCF_3 (^{19}F)	—	−78.45	−78.46	—	−78.37	−78.40

[a] At 298 K, CD_3OD, δ in ppm relative to $SiMe_4$ (^1H) or $CFCl_3$ (^{19}F); s = singlet, d = doublet, dd = doublet of doublets. [b] Four lines are observed at 180 K: δ 3.51, 3.46, 3.38 and 3.33. [c] Coincides with the high-intensity CD_2H pattern of the solvent. [d] Established in a NOE difference experiment.

square-planar arrangement, while a strong preference towards a tetrahedral one is expected.[11] The cation $[Ag\{(SC_4H_3)CMe{=}N]_2C_2H_4\}]^+$ possesses a flattened geometry, even though its ligand bite angle (N–Ag–N) of 77.25(11)° allows a better approximation to a tetrahedron than the 72.4° (average) found in the $[Ag\{[(SC_4H_3)CH{=}N]_2C_6H_{10}\}_2]^+$ cation.[1b] Secondly, the sum of the angles around N^1, 349.1°, indicates that the silver(I) centre is substantially displaced from the plane constituted by the imine function C(5)=N(1) and its α-amino substituent C(7). In the case of a purely sp^2-hybridized N atom the hybrid containing the lone pair is situated in this plane and, since overlap of this filled hybrid with an empty metal orbital is sought, a bonded metal ion is usually expected to reside in the same plane resulting in an angle sum of 360°.[1,7,9–11] We believe that the explanation for this feature is to be found in the intramolecular thiophene ring packing mentioned above since there are no obvious short intermolecular contacts in the crystal structure. In contrast to the significantly flattened silver(I) geometry in $[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}]^+$, the corresponding CuN_4 co-ordination geometry in $[Cu\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2]^+$ is only slightly flattened [Fig. 3(*b*)]. Moreover, the displacement of the copper(I) ion from the imine sp^2 plane is considerably less than in the silver complex where the angles around the imine N atoms add up to 358.0° (average). Nevertheless, the MN_4 co-ordination geometry of each $[M\{[(SC_4H_3)CR{=}N]_2C_2H_4\}_2]^+$ structure is probably best described as a tetrahedron, though in the case of the silver complex cation (R = Me) this is severely compressed.

The difference between the basic co-ordination geometries of the perfectly four-co-ordinated complex cation $[M\{[(SC_4H_3)CR{=}N]_2C_2H_4\}_2]^+$ and the predominantly linearly co-ordinated $[M\{[(SC_4H_3)CH{=}N]_2C_6H_{10}\}_2]^+$ [1b,c] is most likely attributable to the specific shape and relative rigidity of the cyclohexanediyl unit of the N_2S_2 ligand in the latter compound.[7]

Solution Structure of $[M\{[(SC_4H_3)CR{=}N]_2C_2H_4\}_2][O_3SCF_3]$.—The ^{19}F NMR spectra of the $[M\{[(SC_4H_3)CR{=}N]_2C_2H_4\}_2][O_3SCF_3]$ complexes (M = Ag or Cu; R = Me or SC_4H_3) all show one singlet with chemical shifts (Table 2) in a range δ −78.37 to −78.46 that is characteristic for a free, unco-ordinated $^-O_3SCF_3$ anion.[11] Owing to extensive charge delocalization, triflate is a very weak donor and when sufficient other stronger donor functions are present, as in these complexes, it is unlikely to co-ordinate to the metal centre.

The room-temperature ^1H NMR data (Table 2) show marked chemical shift changes upon addition of half an equivalent of the respective metal salts to the $[(SC_4H_3)CR{=}N]_2C_2H_4$ molecules, indicating that complexation takes place. The fact that the differences for Cu^I are larger than for Ag^I may reflect the smaller ionic radius of the former; Cu^I is expected to afford slightly tighter bonded ligands and thus, more pronounced effects.[11] If another half equivalent of $Ag^I(O_3SCF_3)$ is added to the silver(I) complexes the chemical shifts change a little but still only one set of signals is visible, evidencing that the original complexes with an M : L ratio of 1 : 2 undergo rapid ligand exchange at ambient temperatures.

The two separate sets of chemical shifts seen for the thiophene H atoms in the spectra of $[M\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2]^+$ indicate that, on the NMR time-scale, there is no rotation about the imine bond. The nuclear Overhauser effect (NOE) difference spectrum of the $[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2]^+$ cation reveals interactions of the ketimine methyl group with both the ethylenic protons and thiophene H^3. This confirms that, on average, the imine function possesses the *E* configuration and that the thienylmethylene moiety is coplanar, having the sym-*cis* conformation. Together, these observations show the ligand system to have a rather rigid solution structure, which is very similar to that in the solid state.

For all complexes, lowering of the temperature of their solutions does not change the number of pattern sets nor does it substantially affect the chemical shift positions, though the singlets of the ethylenic H atoms undergo a change. About 240 K, broadening becomes noticeable and this increases with further decrease in temperature. This process is reversed by reheating. In the case of the $[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2]^+$ cation, the resonance of the ethylenic H atoms finally decoalesces into a pattern of four separate lines at 180 K. This pattern is attributable to an AA'BB' spin system, and one can conclude that the ligand-dissociation process is no longer taking place and that co-ordination to the silver(I) centre is symmetrical. Experimental problems (low homogeneity, low concentration due to the limited solubility, high-intensity solvent peaks) prevented the observation of similar four-line patterns for the other complexes.

In view of the high similarity of the data we conclude that all these complexes are isostructural. The most likely solution structures of the $[M\{[(SC_4H_3)CR{=}N]_2C_2H_4\}_2]^+$ complex cations are basically identical to the solid-state structures of $[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2]^+$ and $[Cu\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2]^+$, *i.e.* they have more or less a tetrahedral MN_4 co-ordination geometry constituted by two bidentate ligands. There is no evidence that the solution structure of any of the cationic complexes is flattened to the same extent as in the solid-state silver(I) structure.

Experimental

General.—All solvents used in the syntheses of the N_2S_2 compounds were of *p.a.* grade. Methanol and benzene, used in the syntheses of the complexes, were freshly distilled and stored under nitrogen. 2-Acetylthiophene, 1-(2-thienyl)propanone,

Table 3 Crystal data and details of the structure determination

	$[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2][O_3SCF_3]$	$[Cu\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2][O_3SCF_3]$
Formula	$C_{29}H_{32}AgF_3N_4O_3S_5$	$C_{41}H_{32}CuF_3N_4O_3S_9 \cdot CH_3OH$
M	809.79	1069.91
Space group	*Fddd* (no. 70)	$Pca2_1$ (no. 29)
a/Å	16.478(8)	26.337(2)
b/Å	19.56(1)	11.937(4)
c/Å	21.494(9)	28.673(3)
U/Å^3	6927(6)	9014(2)
D_c/g cm^{-3}	1.553	1.577
$F(000)$	3296	4384
μ/cm^{-1}	9.1	9.6
Crystal size/mm	0.45 × 0.35 × 0.28	0.15 × 0.25 × 0.38
T/K	294	100
$\theta_{min}, \theta_{max}$/°	0.95, 25.0	1.4, 25.3
$\Delta\omega$/°	$0.80 + 0.35 \tan\theta$	$0.65 + 0.35 \tan\theta$
hkl ranges	0–19, −23 to 23, 0–25	0–31, 0–14, −25 to 0
Total data	3360	9065
Total unique data (R_{int})	1527 (0.0551)	6524 (0.10)
Observed data	1004 $[I > 2.5\sigma(I)]$	5447 $[I > 2\sigma(I)]$
No. of refined parameters	89	650
Weighting scheme, w^{-1}	$\sigma^2(F)$	$\sigma^2(F_o^2) + (0.188P)^2$
Final R, wR, S; $R1$, $wR2$, S	0.0417, 0.0305, 4.13	0.10, 0.29, 1.005
$(\Delta/\sigma)_{av}$ in final cycle	0.093	0.06
Minimum, maximum electron density/e Å^{-3}	−0.24, 0.42 (near Ag)	−0.92, 3.1

* Details in common: orthorhombic; $Z = 8$; zirconium-filtered Mo-Kα radiation (λ 0.710 73 Å); ω–2θ scans.

Table 4 Final coordinates for non-H atoms of $[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2][O_3SCF_3]$

Atom	x/a	y/b	z/c
Ag(1)	0.125	0.125	0.125
S(1)	0.244 02(8)	−0.006 50(6)	0.106 20(5)
N(1)	0.203 2(2)	0.090 59(16)	0.209 65(15)
C(1)	0.320 8(4)	−0.038 0(3)	0.062 4(3)
C(2)	0.393 0(3)	−0.015 4(3)	0.082 9(3)
C(3)	0.387 9(3)	0.028 4(2)	0.134 2(3)
C(4)	0.309 5(3)	0.038 6(2)	0.153 4(2)
C(5)	0.279 5(3)	0.078 5(2)	0.205 8(2)
C(6)	0.341 4(3)	0.101 8(3)	0.252 5(2)
C(7)	0.170 6(2)	0.127 2(3)	0.263 52(17)

1,2-diaminoethane, toluene-*p*-sulfonic acid and silver(I) trifluoromethanesulfonate were commercially available. 2-Methyl-1-(2-thienyl)propanone, 2,2-dimethyl-1-(2-thienyl)propanone and bis(2-thienyl) ketone were prepared according to a published method for the synthesis of $(SC_4H_3)CMe{=}O$,[12] using commercially available thiophene, acid chlorides and tin(IV) chloride. The compounds $(SC_4H_3)CR{=}O$ (R = Pr^i or Bu^t) were purified by distillation at reduced pressure (10 mmHg, *ca.* 1330 Pa; b.p. 67–69 °C, pale purple oil, yield 75%; and b.p. 69–70 °C, pale green oil, yield 55%, respectively); $(SC_4H_3)_2C{=}O$ was purified by recrystallization from diethyl ether, resulting in ivory needles (m.p. 85–86 °C, yield 40%). Copper(I) trifluoromethanesulfonate–benzene (2/1) was prepared as described in the literature.[13]

Melting points were measured on a model FP1 Mettler apparatus. Proton and ^{19}F NMR spectra of CD_3OD solutions were recorded on a Bruker WM250 spectrometer, with tetramethylsilane as external reference, and a Bruker AC100 spectrometer, with $CFCl_3$ as external reference, respectively. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

Syntheses of $[(SC_4H_3)CR{=}N]_2C_2H_4$.—N,N′-*bis*[1-(2-*thienyl*)*ethylidene*]-1,2-*diaminoethane*. The compound $(SC_4H_3)CMe{=}O$ (9.49 g, 75.3 mmol), 1,2-diaminoethane (2.22 g, 36.9 mmol) and toluene-*p*-sulfonic acid (0.01 g, 0.06 mmol) were dissolved in benzene (75 cm^3) then heated at reflux for 18 h in a Dean–Stark apparatus. After cooling to room temperature, the solvent was evaporated and the remaining solids were dissolved in CH_2Cl_2 (100 cm^3). The CH_2Cl_2 solution was extracted with water–KOH (2 × 100 cm^3, *ca.* 5% w/w) and water (100 cm^3) and then dried over Na_2SO_4 (0.5 h). Subsequent evaporation of the solvent yielded 10 g of an orange solid. Recrystallization from hot methanol and cooling to ambient temperature overnight, gave pure, crystalline $[(SC_4H_3)CMe{=}N]_2C_2H_4$. Yield 6.0 g (60%) of yellow leaflets, m.p. 137–138 °C, [Found (Calc. for $C_{14}H_{16}N_2S_2$): C, 60.80 (60.85); H, 6.05 (5.85); N, 10.10 (10.15); S, 22.95 (23.20%)].

N,N′-*Bis*[*di*(2-*thienyl*)*methylene*]-1,2-*diaminoethane*. The compound $(SC_4H_3)_2C{=}O$ (5.00 g, 25.8 mmol), 1,2-diaminoethane (0.77 g, 12.8 mmol) and toluene-*p*-sulfonic acid (0.01 g, 0.06 mmol) were dissolved in toluene (75 cm^3). After processing this reaction mixture as described above, 5.2 g of the crude product were obtained as a brown solid. Recrystallization from a mixture of methanol (10 cm^3) and CH_2Cl_2 (10 cm^3), which was cooled to 4 °C for 18 h, yielded 3.4 g of pure $[(SC_4H_3)_2C{=}N]_2C_2H_4$ (65%), as light brown needles.

Others. Using the method described for $[(SC_4H_3)CMe{=}N]_2C_2H_4$, the pure ethyl derivative was obtained starting from $(SC_4H_3)CEt{=}O$. Although complete conversion took place, as could be deduced from the amount of water separated, corresponding condensation reactions with $(SC_4H_3)CR{=}O$ (R = Pr^i or Bu^t) did not yield a single product but rather, as evidenced by ^1H NMR spectroscopy, a mixture of compounds (most likely stereoisomers, see Results and Discussion section) from which it proved impossible to separate the desired compound. The use of xylene or mesitylene as solvent, enabling higher reaction temperatures, did not improve this situation. Direct addition of 0.5 equivalent of $Ag^I(O_3SCF_3)$ to a methanolic solution of the mixture in the usual way did not give a pure product. Attempts to obtain the target molecules *via* a template-directed synthesis,[14] by co-ordinating 1,2-diaminoethane to $NiCl_2$ prior to condensation, were also unsuccessful.

Syntheses of the $M^I(O_3SCF_3)$ *Complexes with* M : L = 1 : 2.—$[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2][O_3SCF_3]$. At room temperature, solutions of $[(SC_4H_3)CMe{=}N]_2C_2H_4$ (0.56 g, 2.0 mmol) in MeOH (100 cm^3) and of $Ag^I(O_3SCF_3)$ (0.27 g, 1.1 mmol) in MeOH (100 cm^3) were mixed with exclusion of direct light. Cooling of the resulting solution to 4 °C for 15 h gave 0.54 g

Table 5 Final coordinates for the non-H atoms of $[Cu\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2][O_3SCF_3]$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
Molecule 1							
Cu(1)	0.283 27(7)	0.229 9(2)	0.499 36(11)	C(115)	0.418 4(6)	−0.183 7(14)	0.555 1(6)
S(11)	0.275 3(2)	0.537 0(4)	0.655 2(2)	C(116)	0.449 1(7)	−0.199 8(16)	0.519 9(7)
S(12)	0.186 4(2)	0.325 5(5)	0.551 4(2)	C(117)	0.360 3(7)	0.064 7(15)	0.436 0(6)
S(13)	0.438 1(2)	−0.106 5(4)	0.474 2(2)	C(118)	0.346 2(5)	−0.038 7(11)	0.403 2(5)
S(14)	0.359 9(3)	0.186 1(6)	0.407 2(3)	C(119)	0.340 8(8)	0.027 0(18)	0.354 8(8)
S(15)	0.156 8(2)	−0.177 6(4)	0.491 8(2)	C(120)	0.345 9(9)	0.133(2)	0.358 2(9)
S(16)	0.245 2(2)	0.057 3(5)	0.585 7(2)	C(121)	0.145 4(7)	−0.241 9(15)	0.439 9(6)
S(17)	0.222 1(2)	0.517 5(5)	0.351 4(2)	C(122)	0.177 6(7)	−0.213 2(15)	0.404 7(7)
S(18)	0.342 7(2)	0.456 9(5)	0.469 8(2)	C(123)	0.213 2(7)	−0.125 9(14)	0.419 1(6)
N(11)	0.302 1(5)	0.314 5(11)	0.557 6(5)	C(124)	0.205 0(6)	−0.097 5(13)	0.466 7(6)
N(12)	0.350 7(5)	0.145 0(12)	0.510 1(5)	C(125)	0.227 4(6)	−0.008 7(14)	0.494 4(7)
N(13)	0.236 7(5)	0.094 6(11)	0.479 0(5)	C(126)	0.240 6(6)	−0.033 7(13)	0.542 1(6)
N(14)	0.245 5(5)	0.316 8(10)	0.449 7(5)	C(127)	0.251 8(5)	−0.158 2(11)	0.561 6(5)
C(101)	0.327 9(7)	0.615 2(15)	0.670 7(7)	C(128)	0.264 7(7)	−0.138 9(16)	0.610 3(7)
C(102)	0.366 3(6)	0.602 1(14)	0.642 2(6)	C(129)	0.257 6(9)	−0.034 5(19)	0.626 8(9)
C(103)	0.355 2(7)	0.527 6(15)	0.604 5(7)	C(130)	0.221 2(7)	0.121 9(14)	0.432 0(6)
C(104)	0.306 1(6)	0.483 5(14)	0.607 5(6)	C(131)	0.204 4(7)	0.245 0(15)	0.431 0(7)
C(105)	0.279 7(7)	0.406 6(15)	0.576 5(6)	C(132)	0.245 9(6)	0.416 5(13)	0.435 4(6)
C(106)	0.229 4(7)	0.429 0(14)	0.564 2(6)	C(133)	0.206 6(6)	0.466 5(13)	0.404 7(6)
C(107)	0.205 3(5)	0.548 4(11)	0.559 6(5)	C(134)	0.153 7(6)	0.470 2(14)	0.411 2(6)
C(108)	0.152 3(7)	0.522 0(16)	0.545 3(7)	C(135)	0.128 7(7)	0.514 5(15)	0.373 4(6)
C(109)	0.140 4(7)	0.407 7(16)	0.538 1(7)	C(136)	0.160 1(8)	0.544 6(18)	0.337 2(8)
C(110)	0.355 1(6)	0.286 7(14)	0.571 1(6)	C(137)	0.285 5(6)	0.498 0(14)	0.451 6(6)
C(111)	0.364 8(7)	0.163 2(15)	0.559 2(6)	C(138)	0.276 8(5)	0.627 5(11)	0.453 3(5)
C(112)	0.366 9(6)	0.061 3(12)	0.486 7(5)	C(139)	0.327 7(8)	0.666 5(17)	0.474 6(8)
C(113)	0.393 7(7)	−0.038 1(15)	0.506 4(7)	C(140)	0.363 6(7)	0.580 5(15)	0.480 5(7)
C(114)	0.386 6(5)	−0.089 5(12)	0.552 7(5)				
Molecule 2							
Cu(2)	0.458 02(7)	0.702 4(2)	0.217 26(10)	C(215)	0.306 5(7)	0.289 8(16)	0.175 5(7)
S(21)	0.377 4(2)	0.982 8(5)	0.101 1(2)	C(216)	0.282 9(8)	0.284 2(18)	0.212 9(8)
S(22)	0.556 0(3)	0.795 8(6)	0.166 9(3)	C(217)	0.382 3(7)	0.542 3(17)	0.283 3(7)
S(23)	0.295 5(2)	0.383 6(5)	0.251 2(2)	C(218)	0.391 5(5)	0.447 2(12)	0.316 0(5)
S(24)	0.381 8(2)	0.665 3(5)	0.313 2(2)	C(219)	0.400 3(8)	0.495(2)	0.361 3(9)
S(25)	0.573 3(2)	0.282 2(4)	0.240 3(2)	C(220)	0.394 5(8)	0.604 8(19)	0.362 3(8)
S(26)	0.505 4(2)	0.520 0(4)	0.135 3(2)	C(221)	0.579 9(6)	0.223 6(15)	0.294 3(6)
S(27)	0.490 1(2)	1.003 9(5)	0.368 2(2)	C(222)	0.548 8(7)	0.268 9(15)	0.325 3(7)
S(28)	0.391 5(2)	0.919 9(4)	0.241 8(2)	C(223)	0.518 0(6)	0.358 7(14)	0.308 6(6)
N(21)	0.441 0(5)	0.778 6(11)	0.156 4(5)	C(224)	0.528 1(6)	0.375 7(13)	0.261 7(6)
N(22)	0.389 5(6)	0.618 2(11)	0.207 6(5)	C(225)	0.507 6(6)	0.464 5(14)	0.229 8(6)
N(23)	0.500 6(5)	0.569 0(12)	0.241 9(5)	C(226)	0.495 8(6)	0.428 0(14)	0.180 5(6)
N(24)	0.491 6(6)	0.798 8(12)	0.269 4(6)	C(227)	0.480 4(6)	0.323 3(14)	0.165 6(6)
C(201)	0.387 0(7)	1.068 1(17)	0.055 8(7)	C(228)	0.476 1(6)	0.320 5(15)	0.116 2(6)
C(202)	0.436 2(6)	1.064 0(14)	0.037 9(6)	C(229)	0.487 2(7)	0.422 2(16)	0.096 6(7)
C(203)	0.471 0(6)	0.994 3(14)	0.062 6(6)	C(230)	0.518 5(6)	0.605 9(13)	0.288 6(6)
C(204)	0.439 4(7)	0.941 8(15)	0.102 0(6)	C(231)	0.532 9(6)	0.730 3(13)	0.286 8(6)
C(205)	0.461 9(6)	0.864 4(13)	0.136 6(6)	C(232)	0.486 8(6)	0.897 9(14)	0.283 5(6)
C(206)	0.514 3(6)	0.893 8(13)	0.151 7(6)	C(233)	0.518 2(6)	0.946 2(14)	0.319 6(6)
C(207)	0.534 0(5)	1.016 8(11)	0.159 0(5)	C(234)	0.573 9(6)	0.947 0(14)	0.322 7(6)
C(208)	0.587 7(9)	0.989(2)	0.174 5(9)	C(235)	0.586 2(7)	1.001 8(16)	0.366 4(7)
C(209)	0.599 0(9)	0.883(2)	0.179 6(8)	C(236)	0.545 5(8)	1.030 3(18)	0.394 6(8)
C(210)	0.388 7(6)	0.744 1(13)	0.141 6(6)	C(237)	0.446 7(6)	0.970 1(13)	0.265 2(5)
C(211)	0.377 1(6)	0.625 3(13)	0.158 2(6)	C(238)	0.449 4(5)	1.098 2(11)	0.263 3(5)
C(212)	0.371 1(6)	0.536 5(13)	0.231 5(6)	C(239)	0.398 3(7)	1.130 4(15)	0.242 5(6)
C(213)	0.339 7(6)	0.442 2(14)	0.216 8(7)	C(240)	0.367 9(7)	1.046 2(15)	0.230 3(7)
C(214)	0.345 5(5)	0.383 3(11)	0.170 2(5)				
Triflate anions and MeOH							
S(31)	0.210 0(2)	0.917 5(5)	0.258 4(2)	S(41)	0.500 6(2)	0.405 1(5)	0.469 2(2)
F(31)	0.281 2(5)	0.784 8(12)	0.228 1(5)	F(41)	0.500 0(10)	0.300(2)	0.548 2(10)
F(32)	0.226 8(6)	0.708 7(14)	0.275 8(6)	F(42)	0.539 6(8)	0.213 4(18)	0.491 5(8)
F(33)	0.285 5(6)	0.822 7(14)	0.301 9(6)	F(43)	0.465 8(10)	0.213(2)	0.496 9(10)
O(31)	0.189 1(8)	0.936 3(17)	0.303 1(7)	O(41)	0.547 3(9)	0.460 2(19)	0.480 4(9)
O(32)	0.240 1(6)	1.006 9(13)	0.241 6(6)	O(42)	0.461 2(12)	0.468(3)	0.491 4(12)
O(33)	0.176 1(5)	0.873 9(12)	0.224 3(5)	O(43)	0.472(2)	0.354(5)	0.429(2)
C(31)	0.251 1(9)	0.806 7(19)	0.265 7(8)	C(41)	0.506 3(10)	0.285(2)	0.504 1(10)
O(51)	0.051 2(6)	0.310 4(13)	0.466 3(5)	O(61)	0.222(2)	0.201(5)	0.311(2)
C(51)	0.039 8(10)	0.287(2)	0.419 6(9)	C(61)	0.175(2)	0.208(5)	0.274(2)

(65%) of ivory-coloured crystals [Found (Calc. for $C_{29}H_{32}AgF_3N_4O_3S_5$): C, 42.85 (43.00); H, 4.05 (4.00); N, 6.90 (6.90); S, 19.80 (19.80%)].

The complex $[Ag\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2][O_3SCF_3]$ was prepared *via* the same procedure in 40% yield as a grey solid [Found (Calc. for $C_{41}H_{32}AgF_3N_4O_3S_9$): C, 45.15 (45.50); H, 3.00 (3.00); N, 5.20 (5.20); S, 26.65 (26.65%)].

$[Cu\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2][O_3SCF_3]$. Under an atmosphere of dry nitrogen, a solution of $Cu^I(O_3SCF_3)\cdot 0.5C_6H_6$ (0.62 g, 2.47 mmol) in benzene (40 cm^3) was added to a solution of $[(SC_4H_3)CMe{=}N]_2C_2H_4$ (1.37 g, 4.93 mmol) in benzene (30 cm^3), immediately resulting in a red suspension. After 0.5 h the solvent was filtered off and the remaining solid dissolved in MeOH (20 cm^3). Cooling the red solution to 4 °C for 18 h, gave 1.52 g of dark red crystals (80%) [Found (Calc. for $C_{29}H_{32}CuF_3N_4O_3S_5$): C, 45.25 (45.50); H, 4.25 (4.20); N, 7.35 (7.30); S, 20.85 (20.95%)].

The complex $[Cu\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2][O_3SCF_3]$ was prepared *via* the same procedure in 50% yield as brown crystals [Found (Calc. for $C_{41}H_{32}CuF_3N_4O_3S_9\cdot CH_3OH$): C, 47.80 (47.15); H, 3.20 (3.40); N, 5.10 (5.25); S, 26.85 (26.95%)].

Syntheses of $M^I(O_3SCF_3)$ *Complexes with* $M{:}L \neq 1{:}2$.—All attempts to obtain complexes with stoichiometries other than $M{:}L = 1{:}2$ failed. Even from solutions with a ten-fold excess of the metal salt only the complexes having $M{:}L = 1{:}2$ were isolated. Use of other reaction or recrystallization solvents, *e.g.* pure CH_2Cl_2 or a CH_2Cl_2–hexane mixture, did not make any difference.

Crystallography.—Crystallographic data and numerical details for both complexes are collected in Table 3, final atomic co-ordinates in Tables 4 and 5. X-Ray data were collected on an Enraf-Nonius CAD4 diffractometer for glass fibre-mounted crystals.

$[Ag\{[(SC_4H_3)CMe{=}N]_2C_2H_4\}_2][O_3SCF_3]$. Data were collected for an ivory-coloured block-shaped crystal. Unit-cell parameters were determined from a least-squares treatment of the SET4[14] setting angles of 25 reflections and checked for the presence of higher lattice symmetry.[16] The data were corrected for Lorentz polarization, for a small linear decay (1%) of the intensity-control reflections during 49 h of X-ray exposure time, but not for absorption. The structure was solved by standard Patterson techniques (SHELXS 86)[17] and a series of subsequent Fourier analyses. Refinement on *F* was carried out by full-matrix least-squares techniques. Hydrogen atoms were introduced at calculated positions (C–H 0.98 Å) and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic atomic displacement parameters, H atoms with one common isotropic atomic displacement parameter [$U = 0.102(6)$ Å^2]. The O_3SCF_3 anion is disordered over a crystallographic 222 symmetry site. No discrete structural model of this anion could be fitted on the blurred electron density at this 222 site. The BYPASS procedure[18] was used to take the electron density at the 222 location into account in the subsequent structure-factor and refinement calculations. A total electron count of 581 was found in the unit cell within a total anion accessible area of 1318 Å^3. This corresponds well with the 592 electrons expected for eight anions in the unit cell. Weights based on counting statistics were introduced in the final refinement cycles (after BYPASS). Convergence was reached at $R = 0.0417$, $wR = 0.0305$.

Neutral scattering factors were obtained from ref. 19 and corrected for anomalous dispersion.[20] All calculations were performed with SHELX 76[21] and PLATON[22] (geometrical calculations) on a micro VAX-II cluster.

$[Cu\{[(SC_4H_3)_2C{=}N]_2C_2H_4\}_2][O_3SCF_3]$. X-Ray data were collected at 100 K for a dark red-brown crystal. Unit-cell parameters were derived from the SET4 setting angles[15] of 25 reflections in the range $15 < 2\theta < 26°$. Observed systematic extinctions are consistent with space group *Pcam* or *Pca*2_1. The latter resulted in a successful structure determination and refinement. Data were corrected for Lorentz polarization and absorption (DIFABS;[23] correction range 0.76–1.14). The structure was solved with the PATT option of SHELXS 86[17] and refined on F^2 with SHELXL 93.[24] Hydrogen atoms were taken into account at calculated positions, riding on their carrier atoms. The Cu, S and N atoms were refined with anisotropic atomic displacement parameters. In view of the quality of the data set (related to disorder) the C, O and F atoms were refined with individual isotropic displacement parameters. Several of the thiophene moieties are orientationally disordered as indicated by residual density in the ring plane. A twin parameter [0.68(8)] was included in the refinement to take into account the anomalous scattering associated with this polar space group. A final test for higher symmetry with the MISSYM algorithm as implemented in PLATON[22] indicated that the crystallographically independent molecules are not related by space-group symmetry. The structure contains a small void at (0.124, 0.415, 0.214), however no significant density was found in this area (PLATON/SQUEEZE[23]). Convergence was reached at $R = 0.10$, $wR = 0.29$; these values reflect the rather low intensity of the observed data set and the disorder. Scattering factors were taken from ref. 25.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 (*a*) G. C. van Stein, G. van Koten, F. Blank, L. C. Taylor, K. Vrieze, A. L. Spek, A. J. M. Duisenberg, A. M. M. Schreurs, B. Kojic'-Prodic' and C. Brevard, *Inorg. Chim. Acta*, 1985, **98**, 107; (*b*) G. C. van Stein, G. van Koten, K. Vrieze, A. L. Spek, E. A. Klop, and C. Brevard, *Inorg. Chem.*, 1985, **24**, 1367; (*c*) A. L. Spek, A. J. M. Duisenberg, G. C. van Stein and G. van Koten, *Acta Crystallogr., Sect. C*, 1985, **41**, 374.

2 See, for example, W. S. Emerson and T. M. Patrick, *J. Org. Chem.*, 1949, **14**, 790; G. L. Eichhorn and J. C. Bailar, *J. Am. Chem. Soc.*, 1953, **75**, 2905.

3 G. Lugert, J. Manero, M. Feigel and M. Bremer, *J. Chem. Soc., Chem. Commun.*, 1988, 1395.

4 See, for example, S. Patai, *The Chemistry of the Carbonyl Group*, Interscience, New York, 1966, p. 610; H. Gold, in *Methoden der Organischen Chemie (Houben-Weyl)*, ed. E. Müller, Georg Thieme, Stuttgart, 1976, vol. 7, Part 2b, p. 1951.

5 J. F. Modder, K. Vrieze, G. van Koten and A. L. Spek, *J. Org. Chem.*, 1991, **56**, 5606; A. E. Koziol, R. C. Palenik and G. J. Palenik, *J. Chem. Soc., Chem. Commun.*, 1988, 226.

6 S. C. Bell, G. L. Conklin and S. J. Childress, *J. Am. Chem. Soc.*, 1963, **85**, 2868.

7 J. F. Modder, J.-M. Ernsting, K. Vrieze, M. de Wit, C. H. Stam and G. van Koten, *Inorg. Chem.*, 1991, **30**, 1208.

8 A. L. Spek, PLUTON, Molecular Graphics Program, Utrecht University, The Netherlands, 1995.

9 J. F. Modder, G. van Koten, K. Vrieze and A. L. Spek, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1698.

10 J. F. Modder, K. Vrieze, A. L. Spek, G. Challa and G. van Koten, *Inorg. Chem.*, 1992, **32**, 1238.

11 G. C. van Stein, G. van Koten, K. Vrieze, C. Brevard and A. L. Spek, *J. Am. Chem. Soc.*, 1984, **106**, 4486.

12 J. R. Johnson and G. E. May, *Org. Synth.*, 1943, Coll. Vol. II, 8.

13 R. G. Salomon and J. K. Kochi, *J. Am. Chem. Soc.*, 1973, **95**, 1889.

14 J. Dehand, J. Jordanov and M. Pfeffer, *J. Chem. Soc., Dalton Trans.*, 1976, 1553; D. Sellmann and E. Thallmair, *J. Organomet. Chem.*, 1979, **164**, 337.

15 J. L. de Boer and A. J. M. Duisenberg, *Acta Crystallogr., Sect. A*, 1984, **40**, C410.
16 A. L. Spek, *J. Appl. Crystallogr.*, 1988, **21**, 578.
17 G. M. Sheldrick, SHELXS 86. Program for Crystal Structure Determination, University of Göttingen, 1986.
18 P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 194.
19 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **23**, 321.
20 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
21 G. M. Sheldrick, SHELX 76. Crystal Structure Analysis Package, University of Cambridge, 1976.
22 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.
23 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
24 G. M. Sheldrick, SHELXL 93. Crystal Structure Refinement Package, University of Göttingen, 1993.
25 A. J. C. Wilson (Editor), *International Tables for X-Ray Crystallography*, Kluwer, Dordrecht, 1992, vol. C.

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