S···S Contact-assembled silver(I) complexes of 4,5-ethylenedithio-1,3-dithiole-2-thione having unique supramolecular networks

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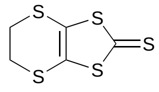
Two silver(I) complexes of 4,5-ethylenedithio-1,3-dithiole-2-thione ($C_5H_4S_5$), $[\{Ag(C_5H_4S_5)_3\}ClO_4\cdot CH_3CN]_2$ and $[Ag(C_5H_4S_5)CF_3SO_3]_\infty$ have been synthesized and characterized crystallographically. They have unique dimeric and two-dimensional structures respectively and are assembled by S···S contacts. The finding of the shortest S···S contacts (3.284 and 3.262 Å) in these complexes indicated that the co-ordination linkage in metal complexes containing these types of sulfur donor compounds could be expected to control the intra- or inter-molecular interactions. The co-ordination mode of the $C_5H_4S_5$ ligand has also been discussed.

In order to achieve the goals of developing advanced materials, for chemists, the past ten years have brought a blossoming of a large field of supramolecular chemistry.[1,2] Intermolecular interactions such as hydrogen bonding, S···S contacts and π–π stacking are efficient organizing forces in supramolecular architecture and the design of new solid-state materials for a number of applications. Many research groups have succeeded in the strategy to control organic molecular aggregation by hydrogen bonding,[3,4] and to synthesize organic conductors assembled by π–π stacking[5–7] or S···S contacts.[8–12] The unique physical properties of these compounds not only depend on the specific molecular properties of the individual components, but are also strongly influenced by the arrangement of interactions within the crystal lattice. In TTF and BEDT-TTF [bis(ethylenedithio)-tetrathiafulvalene] compounds[13–15] and dmit (4,5-disulfanyl-1,3-dithio-2-thionate) complexes $[M(C_3S_5)_2]^{n-}$ [11,12] short S···S contacts were found to play an important role in the conductivity of these sulfur-rich compounds.

However in most of these organic donor–acceptor compounds or organic radical salts, the molecular packing that influences the S···S interaction is mainly controlled by the identity of the molecule itself, the size of the counter ion and co-crystallized solvent molecules.[16] More remarkable is the synthesis of metal complexes of these donor and acceptor compounds, which are assembled by both metal co-ordination bonds and weak molecular interactions. Metal ions have properties of special interest as components of supramolecular systems and linkers for self-assembly. The packing and interaction of organic molecules in the co-ordination compounds have more variety than is observed in pure organic compounds.

To introduce metal ions to these donor–acceptor systems, the sulfur-rich compound 4,5-ethylenedithio-1,3-dithiole-2-thione ($C_5H_4S_5$), which is well known as an electron donor[17] and has available sites to co-ordinate to metal ions, was selected as a ligand in this work. The ligand is also a derivative of C_3S_5 and has a similar structure to half of BEDT-TTF. Silver(I) (d^{10}) ions were used as co-ordination centres and metal bridges because of their affinity for soft sulfur atoms.

Recently we have reported two complexes of $C_5H_4S_5$, $[Ag(C_5H_4S_5)_2NO_3]_\infty$ **3**[18] and $[Cu_4I_4(C_5H_4S_5)_4]_\infty$ **4**.[19] Both of them have a polymeric chain structure bridged by $C_5H_4S_5$ and a S···S contact-assembled network. The shortest S···S contact distances in these two complexes are 3.41 and 3.26 Å respectively. In this paper we report two new silver(I) complexes of $C_5H_4S_5$ with short S···S contacts and the co-ordination chemistry of the ligand. The electronic conductivity of the iodine-doped compounds has also been investigated.



$C_5H_4S_5$

Experimental

General comments

The preparations were performed using Schlenk techniques. The reagent $C_5H_4S_5$ was obtained from Tokyo Kasei Co. and used without further purification. Acetonitrile and tetrahydrofuran were dried and distilled by a standard method before use. Infrared spectra were measured as KBr discs on a JASCO FT/IR 8000 spectrometer and electronic spectra were recorded with a Hitachi 150-20 spectrophotometer. Electrical resistivity was measured by a conventional two-probe method at room temperature with a compressed pellet.

Preparation of the complexes with $C_5H_4S_5$

Dimeric $[\{Ag(C_5H_4S_5)_3\}ClO_4\cdot CH_3CN]_2$ 1. To an acetonitrile solution (4 cm^3) of $C_5H_4S_5$ (44.8 mg, 0.2 mmol) was added $AgClO_4\cdot H_2O$ (22.5 mg, 0.1 mmol) in acetonitrile (4 cm^3). The solution was stirred for 30 min at room temperature under an argon atmosphere. A red precipitate was formed and it was separated and washed with acetonitrile (yield 40%). The filtrate was cooled to −30 °C for one week and after being warmed to room temperature a red oil formed. It was put aside for one month and single crystals for X-ray measurement were obtained (Found: C, 22.16; H, 1.61; N, 1.53. $C_{34}H_{30}Ag_2Cl_2N_2O_8S_{30}$ requires C, 22.16; H, 1.64; N, 1.52%).

Polymeric $[Ag(C_5H_4S_5)CF_3SO_3]_\infty$ 2. To a tetrahydrofuran solution (8 cm^3) of $C_5H_4S_5$ (22.4 mg, 0.1 mmol) was added $AgCF_3SO_3$ (25.7 mg, 0.1 mmol) in tetrahydrofuran (4 cm^3). The solution was stirred for 20 min at room temperature under an argon atmosphere. A red precipitate was formed and it was separated and washed with tetrahydrofuran (yield 56%). Crystals for X-ray measurement were obtained by slow evaporation of the filtrate (Found: C, 15.47; H, 0.85. $C_{12}H_8Ag_2F_6O_6S_{12}$ requires C, 14.97; H, 0.84%).

Iodine-doped compounds. These were prepared by gaseous diffusion. Small amounts of powdered samples of complexes **1** or **2** and solid iodine were separately placed in an H-shaped tube which was then sealed under argon and allowed to stand for 1 month at ambient temperature. Dark brown I_2-doped compounds were obtained.

Table 1 Crystallographic data for the complexes **1** and **2**

	1	**2**
Formula	$C_{34}H_{30}Ag_2Cl_2N_2O_8S_{30}$	$C_{12}H_8Ag_2F_6O_6S_{12}$
Formula weight	1843.06	962.64
Crystal colour, habit	Red, brick	Red, prismatic
Crystal dimensions/mm	0.30 × 0.30 × 0.30	0.30 × 0.30 × 0.20
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	15.334(2)	9.526(2)
b/Å	17.951(3)	18.629(5)
c/Å	12.756(4)	7.7966(8)
α/°	92.85(2)	90.42(2)
β/°	110.53(2)	101.84(1)
γ/°	98.72(1)	100.90(2)
U/Å^3	3229(1)	1328.2(5)
Z	2	2
D_c/g cm^{-3}	1.895	2.407
F(000)	1840.00	936.00
μ(Mo-Kα)/cm^{-1}	17.03	24.88
T/°C	20.0	20.0
$2\theta_{max}$/°	55.0	55.0
No. of total reflections	15 377	6457
No. of unique reflections	14 821	6093
No. of observations $[I > 3\sigma(I)]$	10 959	5260
R^a	0.053	0.035
R'^b	0.075	0.047
Goodness of fit	3.13	1.98
Maximum shift	0.04	0.00
$\Delta\rho_{min}$, $\Delta\rho_{max}$/e Å^{-3}	−1.22, 1.39	−1.54, 0.49

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ where $w = 4F_o^2/\Sigma\sigma^2(F_o^2)$.

X-Ray crystallography

X-Ray diffraction experiments were performed at room temperature on a Rigaku AFC-7R diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å). Unit-cell parameters were obtained from a least-squares refinement using the setting angles of 25 reflections. Intensity data were collected by using standard scan techniques (ω–2θ). An empirical correction based on azimuthal scans of several reflections was applied and the data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods (MITHRIL 84 for **1** and MULTAN 88 for **2**)[20,21] and expanded using Fourier techniques (DIRDIF 94).[22] The final full-matrix least-squares refinements for these structures were performed on these data having $I > 3.00\sigma(I)$. For complex **1** the perchlorate anions were refined isotropically for the disorder, while the rest of the non-hydrogen atoms were refined anisotropically. All the non-hydrogen atoms were refined anisotropically for complex **2**. Hydrogen atoms of the two complexes were included but not refined. All crystallographic computations were performed on an INDY computer using the TEXSAN program system.[23] Details of crystal data are summarized in Table 1.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/521.

Results and Discussion

Spectroscopic studies of the complexes

The IR spectra of complexes **1** and **2** show significant changes in the range 1000–1100 cm^{-1} [ν(C–S) stretching frequency of the heterocyclic ring]. The C=S stretching frequency of 1477 cm^{-1} for the free dithiole–thione[24] is split into three bands. The main peaks for ν(C–S) are 1451 cm^{-1} for **1** and 1453 cm^{-1} for **2**, similar to that of the silver nitrate complex $[Ag(C_5H_4S_5)_2NO_3]_\infty$.[18] The characteristic broad peaks of the perchlorate anion (1088 cm^{-1}) and the triflate anion (1254 cm^{-1}) are also shown in the IR spectra of the complexes.

Table 2 Selected bond lengths (Å) and angles (°) for $[\{Ag(C_5H_4S_5)_3\}ClO_4{\cdot}CH_3CN]_2$ **1**

Ag(1)–S(1)	2.535(1)	Ag(1)–S(6)	2.543(2)
Ag(1)–S(11)	2.474(2)	Ag(1)–S(16)	2.906(2)
Ag(2)–S(16)	2.567(2)	Ag(2)–S(21)	2.477(2)
Ag(2)–S(26)	2.540(1)	Ag(2)–S(6)	3.043(2)
S(1)–C(1)	1.678(5)	S(6)–C(6)	1.673(5)
S(11)–C(11)	1.679(5)	S(16)–C(16)	1.686(5)
S(21)–C(21)	1.666(5)	S(26)–C(26)	1.660(5)
S(1)–Ag(1)–S(6)	95.99(5)	S(1)–Ag(1)–S(11)	118.86(5)
S(6)–Ag(1)–S(11)	131.41(6)	S(16)–Ag(2)–S(21)	139.07(5)
S(16)–Ag(2)–S(26)	93.33(4)	S(21)–Ag(2)–S(26)	121.31(5)

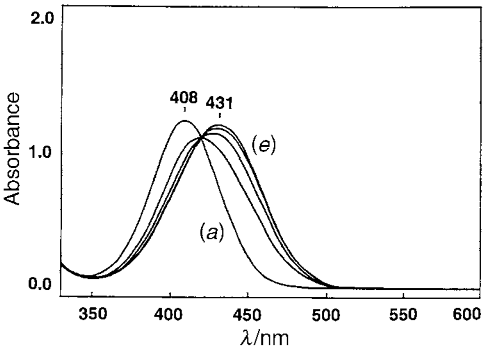


Fig. 1 The electronic spectra of titrating a solution of $C_5H_4S_5$ in acetone (1.0 × 10^{-4} mol dm^{-3}) with a solution of $AgClO_4$ (*a*) 0.0, (*b*) 0.5 × 10^{-1}, (*c*) 1.0 × 10^{-1}, (*d*) 1.5 × 10^{-1} and (*e*) 2.0 × 10^{-1} mol dm^{-3} in acetone

Titration of a solution of $C_5H_4S_5$ in acetone (1.0 × 10^{-4} mol dm^{-3}) with excess $AgClO_4$ in the same solvent clearly showed the shift of the π–π* band of the ligand (408 ⟶ 431 nm, Fig. 1). The isosbestic point appeared at 420 nm suggesting that there are only two species existing in the system besides the silver perchlorate. One is the ligand and the other must be $[Ag(C_5H_4S_5)_3]^+$. The equilibrium is $Ag^+ + 3C_5H_4S_5 \rightleftharpoons Ag(C_5H_4S_5)_3^+$, even in excess silver ion concentration. This is the reason why excess silver salts were used in the synthesis of the silver complexes.

Crystal structure of $[\{Ag(C_5H_4S_5)_3\}ClO_4{\cdot}CH_3CN]_2$ 1

An ORTEP[25] view of the complex $[\{Ag(C_5H_4S_5)_3\}ClO_4{\cdot}CH_3CN]_2$, with selected atom labelling is shown in Fig. 2(*a*) (perchlorate anion and acetonitrile molecule which do not co-ordinate to the metal ion are omitted for clarity). The selected bond distances and angles are listed in Table 2. The molecule is assembled by two unidentical $[Ag(C_5H_4S_5)_3]ClO_4{\cdot}CH_3CN$ moieties. Each Ag^I ion is co-ordinated to three $C_5H_4S_5$ molecules through thiocarbonyl sulfur atoms (C=S) in a quasi-triangle geometry. The silver–sulfur bond distances are in the range 2.474–2.567 Å, within that expected for Ag–S (thiocarbonyl sulfur).[26] The bond angles around the Ag(1) atoms, S(1)–Ag(1)–S(6), S(6)–Ag(1)–S(11), S(1)–Ag(1)–S(11) are 95.99(5), 131.41(6) and 118.86(5)° respectively and sum to 346.26°. Similarly the bond angles around the Ag(2) atoms, S(16)–Ag(2)–S(21), S(21)–Ag(2)–S(26), S(16)–Ag(2)–S(26) are 139.07(5), 121.31(5) and 93.33(4)° respectively and sum to 353.71°. These data show some distortion from the sum of 360° for ideal trigonal geometry. Owing to the weak co-ordination linkage between the pair of $[Ag(C_5H_4S_5)_3]^+$, both Ag(1) and Ag(2) atoms lie out of the trigonal planes and are close to each other [Fig. 2(*b*)]. The Ag(1)–S(16) (2.91 Å) and Ag(2)–S(6)

Table 3 Selected bond lengths (Å) and angles (°) for $[Ag(C_5H_4S_5)CF_3SO_3]_\infty$ **2**

Ag(1)–S(1)	2.5495(9)	Ag(1)–S(6)	2.584(1)
Ag(1)–S(1′)	2.920(1)	Ag(1)–S(6′)	2.894(1)
Ag(1)–O(3′)	2.621(3)	Ag(2)–S(4)	2.596(1)
Ag(2)–S(8′)	2.841(1)	Ag(2)–O(1)	2.509(3)
Ag(2)–O(4)	2.409(3)	Ag(2)–O(6)	2.454(4)
S(1)–C(1)	1.688(3)	S(6)–C(6)	1.679(4)
S(1′)–Ag(1)–S(6′)	166.34(3)	S(1)–Ag(1)–S(6)	137.63(3)
S(6)–Ag(1)–O(3′)	128.49(7)	S(1)–Ag(1)–O(3′)	93.85(7)
S(4)–Ag(2)–S(8)	107.65(3)	S(4)–Ag(2)–O(1)	96.87(7)
S(4)–Ag(2)–O(4)	119.9(1)	S(4)–Ag(2)–O(6)	118.85(9)

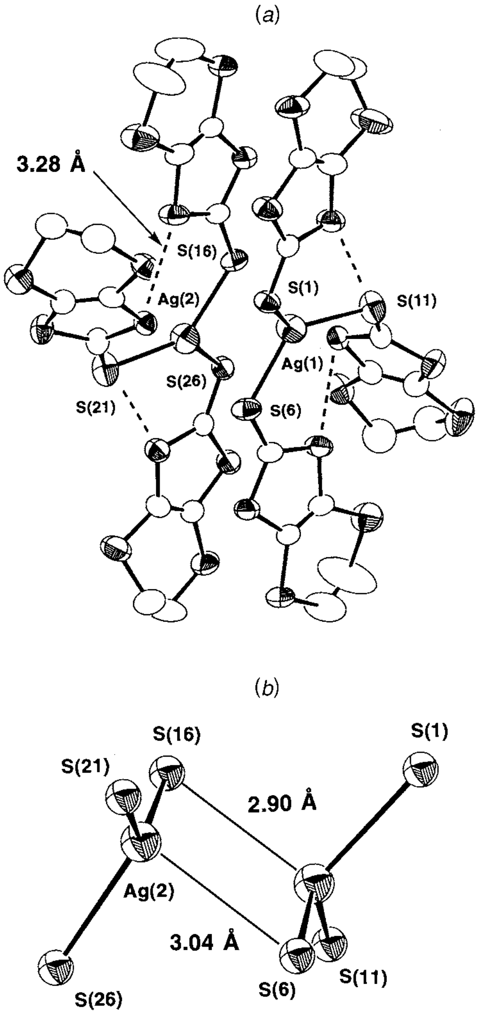


Fig. 2 (*a*) An ORTEP view of the dimeric structure of $\{[Ag(C_5H_4S_5)_3]_2\}^{2+}$; (*b*) co-ordination sphere of the complex

(3.04 Å) distances are somewhat longer than ordinary Ag–S distances, but can still be assigned as weak co-ordination bonds.[26] The Ag(1)–Ag(2) separation of 3.35 Å is longer than the metal–metal bond of metallic silver. Thereby complex **1** has a dimeric structure with two weak inter-co-ordinated quasi-trigonal $[Ag(C_5H_4S_5)_3]^+$ moieties.

The S···S contacts in **1** exist both intra- and intermolecularly and are less than the sum of van der Waals radii of two S atoms (3.60 Å). In **1** the shortest contact is 3.284 Å [intramolecular contact, Fig. 2(*a*)]. Since the average S···S contact distances of highly conductive compounds of TTF, BEDT-TTF and their derivatives are about 3.50 Å, the distance of 3.28 Å here is a rare example. Fig. 3 shows the molecular packing and the one-dimensional intermolecular S···S contacts.

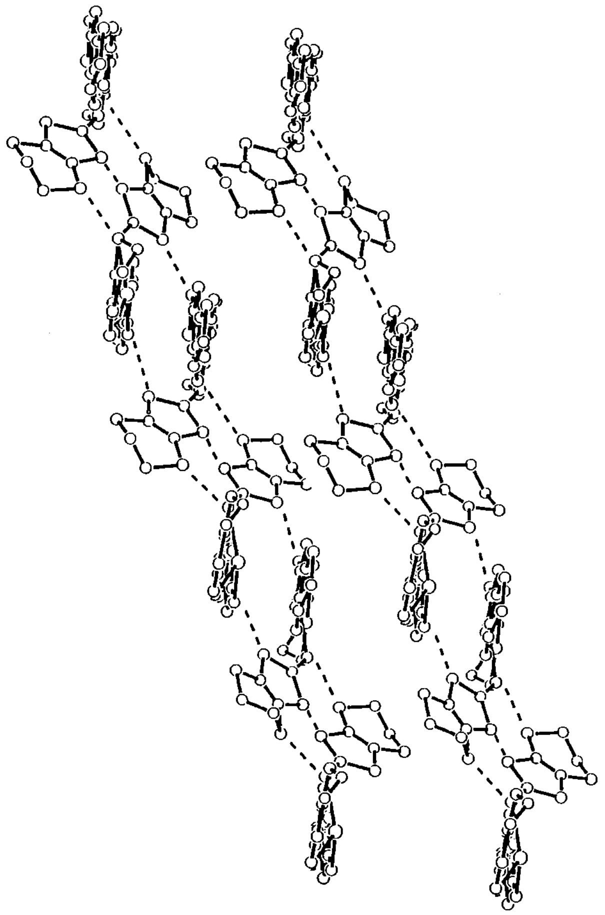


Fig. 3 Molecular packing and the one-dimensional intermolecular S···S contacts of $[\{Ag(C_5H_4S_5)_3\}ClO_4{\cdot}CH_3CN]_2$

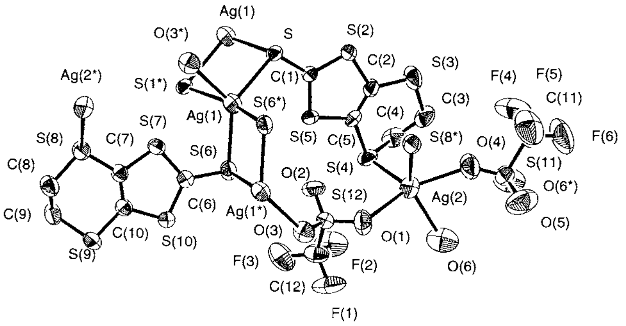


Fig. 4 An ORTEP view of the complex $[Ag(C_5H_4S_5)CF_3SO_3]_\infty$

Crystal structure of $[Ag(C_5H_4S_5)CF_3SO_3]_\infty$ 2

The anion $CF_3SO_3^-$ is able to co-ordinate and it does so by bridging silver(I) atoms in the complex $[Ag(C_5H_4S_5)CF_3SO_3]_\infty$ to form a two-dimensional polymer structure. There are two crystallographically independent silver(I) atoms. Although both Ag(1) and Ag(2) involve a five-co-ordinate environment, Ag(1) has a S_4O donor set and is co-ordinated by four thiocarbonyl sulfur atoms of four separate $C_5H_4S_5$ molecules and one oxygen atom of a triflate anion, whereas Ag(2) is bonded to a S_2O_3 donor set by two thioether sulfur atoms and three oxygen atoms of triflate anions. An ORTEP view of complex **2** with atom labelling is shown in Fig. 4. Selected bond distances and angles are given in Table 3.

Stereochemistry of silver(I) complexes is dominated by four- and three-co-ordination. In contrast five-co-ordinate silver(I) compounds are unusual. In complex **2**, the Ag(1) centre is in a distorted trigonal-bipyramidal geometry where the trigonal plane is defined by atoms S(1), S(6) and O(3) with distances 2.5495(9), 2.584(1) and 2.621(3) Å, respectively. The Ag(1)

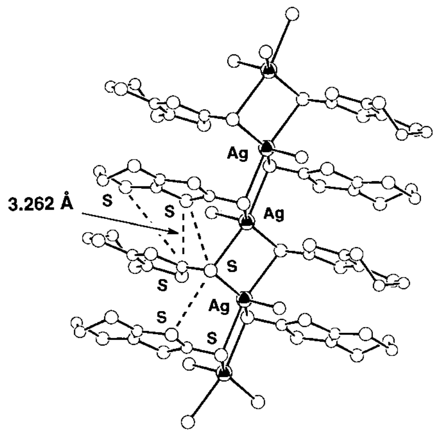


Fig. 5 Thiocarbonyl sulfur bridged chain structure of Ag(1) atoms [triflate and Ag(2) atoms are omitted for clarity]

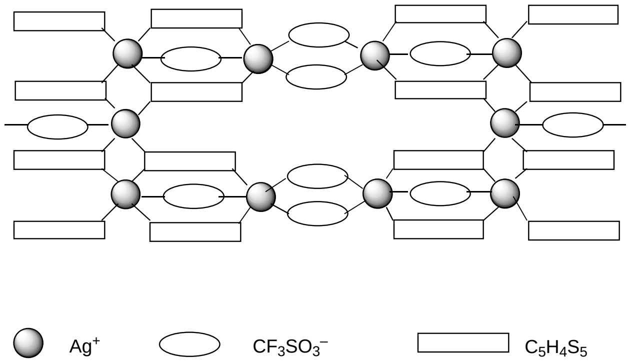


Fig. 6 Schematic structure of the two-dimensional network of $[Ag(C_5H_4S_5)CF_3SO_3]_\infty$

atom also forms Ag–S bonds to two axial donor atoms S(1′) and S(6′) with longer distances of 2.920(1) and 2.894(1) Å. On the other hand, the Ag(2) co-ordination centre forms a distorted square-pyramidal geometry. The Ag–O distances of 2.409(3), 2.454(4) and 2.509(3) Å are shorter than that in other triflate complexes of silver(I).[27,28] The Ag(2)–S(8) bond distance of 2.841(1) Å is a rather weak one, comparable to that in $[Ag(C_5H_4S_5)_2NO_3]_\infty$. However, the axial co-ordination of S(4) (thioether type) to Ag(2) is unexpectedly strong with a distance of 2.596(1) Å.

The Ag(1) atoms are doubly-bridged by thiocarbonyl sulfur atoms of the ligands to form parallel one-dimensional chains along the *c* axis [Fig. 5, the triflate and Ag(2) atoms are omitted for clarity]. All the ligands are approximately perpendicular to the chain and S···S contacts are found between them, the shortest being 3.262 Å. Therefore this chain is also connected by S···S contacts. These chains are subsequently linked by Ag(2) and triflate anions to give a two-dimensional polymer structure, Fig. 6 gives a schematic view of this network.

Co-ordination chemistry of $C_5H_4S_5$

Until now, the only reported complex of $C_5H_4S_5$ by other researchers is an antimony complex $SbCl_3(C_5H_4S_5)_{1.5}$.[24] Including the two previously reported complexes, *i.e.* $[Ag(C_5H_4S_5)_2NO_3]_\infty$ **3**[18] and $[Cu_4I_4(C_5H_4S_5)_4]_\infty$ **4**,[19] a total of four new complexes containing this ligand have been synthesized and characterized crystallographically by our group. Thereby the co-ordination modes of the $C_5H_4S_5$ ligand can be classified into four types: monodentate co-ordination by the thiocarbonyl group (type **I**) as in $[Cu_4I_4(C_5H_4S_5)_4]_\infty$; bridge formation by the sulfur of the thiocarbonyl group (type **II**) as in $SbCl_3(C_5H_4S_5)_{1.5}$; bidentate co-ordination by both the thiocarbonyl group and the thioether group (type **III**) as in $[Ag(C_5H_4S_5)_2NO_3]_\infty$ and $[Cu_4I_4(C_5H_4S_5)_4]_\infty$; tridentate co-ordination by the thiocarbonyl sulfur (acting as a bridge) and the thioether sulfur (type **IV**) as in the complex $[Ag(C_5H_4S_5)CF_3SO_3]_\infty$. The complex $[\{Ag(C_5H_4S_5)_3\}ClO_4\cdot CH_3CN]_2$ has mainly co-ordination of type **I** and if the weak linkage within the dimer is considered, the co-ordination can be classed as type **II**. The co-ordination types are schematically summarized in Fig. 7 and Table 4. With the exception of type **I**, the other co-ordination types usually give polymeric structures.

Table 4 Co-ordination type and sulfur–metal distances (Å) of complexes containing $C_5H_4S_5$

Complex	Type	M–S (thiocarbonyl)	M–S (thioether)
$[\{Ag(C_5H_4S_5)_3\}ClO_4\cdot CH_3CN]_2$	**I** (**II**)	2.474–2.567	
$[Ag(C_5H_4S_5)CF_3SO_3]_\infty$	**IV**	2.549, 2.584	2.841, 2.596
$[Ag(C_5H_4S_5)_2NO_3]_\infty$[16]	**III**	2.561	2.827
$[Cu_4I_4(C_5H_4S_5)_4]_\infty$[17]	**I**, **III**	2.292, 2.280	2.432
$SbCl_3(C_5H_4S_5)_{1.5}$[22]	**II**	3.085–3.407	

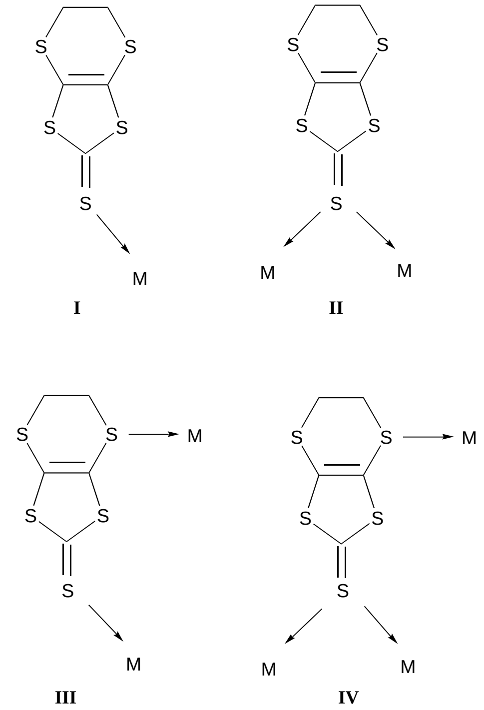


Fig. 7 Co-ordination types of the ligand $C_5H_4S_5$

The ethylene group in the six-membered ring of $C_5H_4S_5$ is not conjugated with the other atoms of the ligand and has a distorted conformation similar to BEDT-TTF. In type **I** co-ordination, the anisotropic displacement parameters of the ethylene group are generally very high, such as in the complex $[\{Ag(C_5H_4S_5)_3\}ClO_4\cdot CH_3CN]_2$ [Fig. 2(*a*)]. This disorder is also found in the complex $[Cu_4I_4(C_5H_4S_5)_4]_\infty$[19] and is a common phenomenon in BEDT-TTF compounds.[29] However, this disorder can be largely reduced if the sulfur atoms in the six-membered ring co-ordinate as in complexes **2**, **3** and **4** (co-ordination types **III** or **IV**).

Most of the compounds of TTF and BEDT-TTF and their analogues are not involved in direct co-ordination to the metal ions. Only two examples, namely (BEDT-TTF)Cu_2Br_3 and $[Rh_2(O_2CCH_3)_4(TTF)_2]$[30,31] in which the sulfur atom in the five- or six-membered ring directly co-ordinates to metal atoms have been reported. Continuing these findings, the three complexes **2**, **3** and **4** reported by our group have been found to have co-ordination of the thioether sulfur in the six-membered ring of $C_5H_4S_5$. It is noted that the Ag–S (thioether) distances are longer than the Ag–S (thiocarbonyl) distances (Table 4), therefore the co-ordination of thioether sulfur in the six-membered

Table 5 S · · · S Contact distances (Å) for complexes **1** and **2**

$[\{Ag(C_5H_4S_5)_3\}ClO_4{\cdot}CH_3CN]_2$			
S(1)–S(22)	3.514(2)	S(1)–S(11′)	3.524(2)
S(2)–S(11)	3.573(2)	S(4)–S(25′)	3.585(3)
S(6)–S(25′)	3.549(2)	S(7)–S(13)	3.440(2)
S(11)–S(23′)	3.447(2)	S(12)–S(23′)	3.504(2)
S(13)–S(26)	3.317(2)	S(14)–S(30′)	3.390(3)
S(15)–S(23′)	3.545(2)	S(18)–S(22)	3.284(2)
S(21)–S(28)	3.492(2)	S(21)–S(26′)	3.493(2)
$[Ag(C_5H_4S_5)CF_3SO_3]_\infty$			
S(1)–S(9′)	3.393(1)	S(1)–S(7′)	3.589(1)
S(2)–S(7′)	3.262(1)	S(2)–S(8′)	3.530(1)

ring is weaker than that of the thiocarbonyl group. Resonance structures of $C_5H_4S_5$ are shown in the paper by Drew *et al.*[24] The terminal sulfur of the C=S group lies in an electron-rich environment and the other sulfur atoms are in a partially conjugated state. The weak co-ordination ability of the thioether-type sulfur atoms may be due to the partial conjugation of the electrons in the π-system. The ether-type sulfur in the five-membered ring is more difficult to co-ordinate to the metal ion than that in the six-membered ring. The unusually short Ag(2)–S(4) (ether type) distance of 2.596 Å in complex **2** is presumably formed because of the weaker co-ordination of the other atoms.

S · · · S Contacts of the complexes

Supermolecules built from smaller molecules mainly involve intermolecular interactions. On the other hand, with polymeric molecules the supramolecular association may be either intermolecular occurring between low dimensional structures or intramolecular involving function sites located in the polymer. The S · · · S contacts in the dimer complex **1** form a one-dimensional chain, and the S · · · S interactions of **2** give the two-dimensional network.

The short S · · · S distances for complexes **1** and **2** are listed in Table 5. The 'side-by-side' or 'up–down' arrangement of $C_5H_4S_5$ molecules with short S · · · S distances indicates an efficient intermolecular π–π orbital interaction, which forms a broadened energy band over the whole lattice. Most of the TTF and C_3S_5 based superconductors have this character. It is known that the stronger the S · · · S contact, the more effective is the increase in the conductivity. When the temperature is decreased or the pressure increased, the S · · · S distance is shorter than in ambient conditions and accordingly the conductivity is increased.[32]

In general, the S · · · S contact distances are in the range 3.35–3.65 Å. An unusually short S · · · S contact of 3.23 Å which results from the Pt–Pt bond in a dimeric structure has been found in $TTF[Pt(C_3S_5)_2]_3$.[33] Another example is $TTF[Pd(C_3S_5)_2]_2$,[34] the shortest S · · · S distance of 3.26 Å also being due to metal–metal bonding. In the case of complexes of $C_5H_4S_5$, the unusually short distances of 3.284 Å for **1** and 3.262 Å for **2** are attributable to the co-ordination bond linkage. In complex **4** the shortest distance of 3.257(2) Å between polymeric chains only occurs as a result of the effect of the molecular packing.[19]

To date, many conductive sulfur-rich compounds were designed by modification of the anion and the co-crystallized solvent molecules to change the crystal phase and molecular interactions.[16] However, this is a poorly understood and difficult to control 'self-assembly' process. Co-ordination linkage or co-ordination chemistry is a well known field, therefore it is possible to control the design of complexes in which the metal atom is directly co-ordinated to derivatives of TTF or BEDT-TTF.

The S · · · S contact is one of the most important factors by which the sulfur-rich compounds exhibit high conductivity. Another important feature of the conductive compounds is that the constituent molecules are in a mixed-valence state (partial-oxidation, -reduction or charge-transfer). Halogen-doping of the conjugated electron donor has been shown to be an effective strategy for the synthesis of electronically conductive compounds.[35,36] The complexes **1** and **2** were partially oxidized by iodine-doping. Although the complexes and the iodine-doped free $C_5H_4S_5$ are insulators ($\sigma < 10^{-12}$ S cm^{-1}), the iodine-doped products of complexes **1** and **2** behave as semiconductors with conductivities of 6.9×10^{-5} and 1.5×10^{-4} S cm^{-1} respectively at room temperature.

Conclusion

After having reported the complexes $[Ag(C_5H_4S_5)_2NO_3]_\infty$ and $[Cu_4I_4(C_5H_4S_5)_4]_\infty$, we have succeeded in the synthesis and characterization of two new complexes of 4,5-ethylenedithio-1,3-dithiole-2-thione with d^{10} metals, *i.e.* $[\{Ag(C_5H_4S_5)_3\}ClO_4{\cdot}CH_3CN]_2$ and $[Ag(C_5H_4S_5)CF_3SO_3]_\infty$. Unique dimers, and one- and two-dimensional structures were found. Furthermore, with the co-operation of co-ordination bonds and S · · · S contacts they are assembled to form one-, two- and three-dimensional supermolecules. The main findings of this study are: (1) the co-ordination chemistry of the $C_5H_4S_5$ ligand has been systematically explored with the finding of three new co-ordination types for this ligand (**I**, **III** and **IV**); (2) the finding of the shortest S · · · S contacts (3.284 for **1** and 3.262 Å for **2**) indicates that the co-ordination linkage in metal complexes with organic donors can be expected to control the intra- or inter-molecular interactions of supermolecules and that may be an important strategy in the search for new materials and crystal engineering.

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References

1 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.
2 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304.
3 J. C. MacDonald and G. M. Whitesides, *Chem. Rev.*, 1994, **94**, 2383.
4 C. B. Aakeroy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, **22**, 397.
5 M. Kato, K. Sasano, C. Kosuge, M. Yamazaki, S. Yano and M. Kimura, *Inorg. Chem.*, 1996, **35**, 116.
6 M. Munakata, T. Kuroda-Sowa, M. Maekawa, M. Nakamura, S. Akiyama and S. Kitagawa, *Inorg. Chem.*, 1994, **33**, 1284.
7 M. Munakata, J. Dai, M. Maekawa, T. Kuroda-Sowa and J. Fukui, *J. Chem. Soc., Chem. Commun.*, 1994, 2331.
8 M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Hirota and S. Kitagawa, *Inorg. Chem.*, 1995, **34**, 2705.
9 J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn, A. J. Schultz and M. Whangbo, *Prog. Inorg. Chem.*, 1987, **35**, 1.
10 M. R. Bryce, *Chem. Soc. Rev.*, 1991, **20**, 355.
11 R. M. Olk, B. Olk, W. Dietzsch, R. Kirmse and E. Hoyer, *Coord. Chem. Rev.*, 1992, **117**, 99.
12 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115.
13 B. A. Scott, S. J. L. Placa, J. B. Torrance, B. D. Silverman and B. Welber, *J. Am. Chem. Soc.*, 1977, **99**, 6631.
14 C. K. Johnson and C. R. Watson, *J. Chem. Phys.*, 1976, **64**, 2271.
15 H. Mori, S. Tanaka, T. Mori and Y. Maruyama, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1136.
16 J. A. Schlueter, J. M. Willams, U. Geiser, H. H. Wang, A. M. Kini, M. Kelly and J. D. Dudek, *Mol. Cryst. Liq. Cryst.*, 1996, **285**, 43.
17 N. Svenstrup and J. Becher, *Synthesis*, 1995, 215.
18 J. Dai, M. Munakata, T. Kuroda-Sowa, Y. Suenaga, L. P. Wu and M. Yamamoto, *Inorg. Chim. Acta*, 1997, **255**, 163.
19 J. Dai, M. Munakata, L. P. Wu, T. Kuroda-Sowa and Y. Suenaga, *Inorg. Chim. Acta*, 1997, in the press.
20 C. J. Gilmore, MITHRIL 84, An Integrated Direct Methods Computer Program, University of Glasgow, 1984.

21 T. Debaerdemaeker, G. Germain, P. Main, L. S. Refaat, C. Tate and M. M. Woolfson, MULTAN 88, Structure Determination Package, University of York, 1988.

22 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, DIRDIF 94, Technical Report of the Crystallographic Laboratory, University of Nijmegen, 1994.

23 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1992.

24 M. G. B. Drew, J. M. Kisenyi and R. V. Parish, *J. Chem. Soc., Dalton Trans.*, 1987, 1605.

25 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

26 R. J. Lancashire, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, New York, 1987, vol. 5, pp. 775–859.

27 T. Suzuki, H. Kotsuki, K. Isobe, N. Moriya, Y. Nakagawa and M. Ochi, *Inorg. Chem.*, 1995, **34**, 530.

28 K. A. Hirsch, D. Venkataraman, S. R. Wilson, J. S. Moore and S. Lee, *J. Chem. Soc., Chem. Commun.*, 1995, 2199.

29 J. M. Williams, A. J. Schultz, U. Geiser, K. D. Carlson, A. M. Kini, H. H. Wang, W. Kwok, M. Whanbo and J. E. Schirber, *Science*, 1991, **252**, 1501.

30 M. B. Inoue, M. Inoue, M. A. Bruck and Q. Fernando, *J. Chem. Soc., Chem. Commun.*, 1992, 515.

31 G. Matsubayashi, K. Yokoyama and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1988, 3059.

32 H. Mori, S. Tanaka, M. Oshima, G. Saito, T. Mori, Y. Maruyama and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2183.

33 M. Bousseau, L. Valade, J. Legros, P. Cassoux, M. Gardauskas and L. V. Interrante, *J. Am. Chem. Soc.*, 1986, **108**, 1908.

34 J. Legros and L. Valade, *Solid State Commun.*, 1988, **68**, 599.

35 J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffmann and T. J. Marks, *J. Am. Chem. Soc.*, 1977, **99**, 287.

36 M. Cowie, A. Gleizes, G. W. Grynkwich, D. W. Kalina, M. S. McClure, R. P. Scaringe, R. C. Teitelbaum, S. L. Ruby, J. A. Ibers, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2921.

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