Silver(I) nitrate two-dimensional coordination polymers of two new pyrazinethiophane ligands: 5,7-dihydro-1H,3H-dithieno[3,4-b:3′,4′-e]pyrazine and 3,4,8,10,11,13-hexahydro-1H,6H-bis([1,4]dithiocino)[6,7-b:6′,7′-e]pyrazine

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The two new pyrazineophanes, 5,7-dihydro-1H,3H-dithieno[3,4-b:3′,4′-e]pyrazine, $C_8H_8N_2S_2$, **L1**, and 3,4,8,10,11,13-hexahydro-1H,6H-bis([1,4]dithiocino)-[6,7-b:6′,7′-e]pyrazine, $C_{12}H_{16}N_2S_4$, **L2**, both crystallize with half a molecule in the asymmetric unit; the whole molecules are generated by inversion symmetry. The molecule of **L1**, which is planar (r.m.s. deviation = 0.008 Å), consists of two sulfur atoms linked by a rigid tetra-2,3,5,6-methylenepyrazine unit, forming planar five-membered rings. The molecule of **L2** is step-shaped and consists of two S–CH₂–CH₂–S chains linked by the central rigid tetra-2,3,5,6-methylenepyrazine unit, forming eight-membered rings that have twist-boat-chair configurations. In the crystals of both compounds, there are no significant intermolecular interactions present. The reaction of **L1** with silver nitrate leads to the formation of a two-dimensional coordination polymer, poly[(μ-5,7-dihydro-1H,3H-dithieno[3,4-b;3′,4′-e]pyrazine-$\kappa^2 S$:$S′$)(μ-nitrato-$\kappa^2 O$:$O′$)-silver(I)], $[Ag(NO_3)(C_8H_8N_2S_2)]_n$, (**I**), with the nitrato anion bridging two equivalent silver atoms. The central pyrazine ring is situated about an inversion center and the silver atom lies on a twofold rotation axis that bisects the nitrato anion. The silver atom has a fourfold AgO_2S_2 coordination sphere with a distorted shape. The reaction of **L2** with silver nitrate also leads to the formation of a two-dimensional coordination polymer, poly[[$\mu_3$3,4,8,10,11,13-hexahydro-1H,6H-bis([1,4]dithiocino)[6,7-b;6′,7′-e]pyrazine-$\kappa^3 S$:$S′$:$S′′$](nitrato-κO)-silver(I)], $[Ag(NO_3)(C_{12}H_{16}N_2S_4)]_n$, (**II**), with the nitrate anion coordinating in a monodentate manner to the silver atom. The silver atom has a fourfold $AgOS_3$ coordination sphere with a distorted shape. In the crystals of both complexes, the networks are linked by C—H⋯O hydrogen bonds, forming supramolecular frameworks. There are additional C—H⋯S contacts present in the supramolecular framework of **II**.
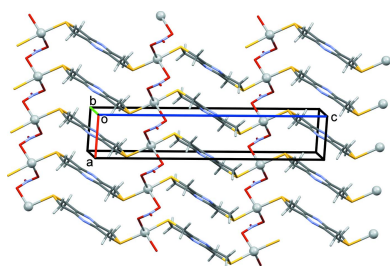
1. Chemical context

Ligands with mixed hard and soft binding characters, such as N and S donor atoms, are known to display diverse coordination properties, either by binding selectively to metal centers or by coordination to a wide range of metal cations giving rise to unusual coordination geometries. The title compounds 5,7-dihydro-1H,3H-dithieno[3,4-b:3′,4′-e]pyrazine (**L1**), and 3,4,8,10,11,13-hexahydro-1H,6H-bis([1,4]dithiocino)[6,7-b:-6′,7′-e]pyrazine (**L2**), are new N_2S_x (x = 2 in **L1** and = 4 in **L2**) ligands designed for the formation of coordination polymers (Assoumatine, 1999). In **L1**, both the nitrogen and sulfur

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potential coordination sites are orientated *exo* to their respective rings. Because of this and the rigidity of the entire molecule, the potential chelating ability appears compromised, as stated by Shimizu and colleagues, who prepared a number of Ag^I polymer networks with the benzene analogue of **L1**, 5,7-dihydro-1*H*,3*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene (Shimizu *et al.*, 1998; 1999; Melcer *et al.*, 2001). A search of the Cambridge Structural Database (Groom *et al.*, 2016) revealed that **L2** is unique and no benzene analogue or complexes of this analogue have been described. Using the nomenclature of the group of Shim Sung Lee (Siewe *et al.*, 2014; Kim *et al.*, 2016, 2018), **L2** can be described as the bis-*ortho*-L regioisomer. Although, in view of the small size of the macrocycles, it is unlikely that either a *meta*- or a *para*-bis-L regioisomer could be formed.

L1

L2
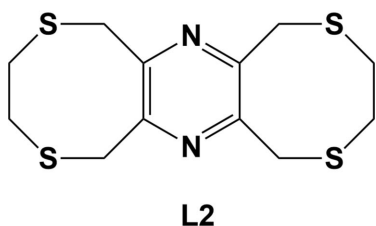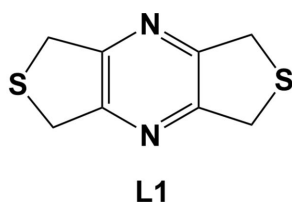
2. Structural commentary

The molecular structure of ligand **L1** is illustrated in Fig. 1. The molecule possesses inversion symmetry and consists of two sulfur atoms linked by a rigid tetra-2,3,5,6-methylene-pyrazine unit. The molecule is planar (r.m.s. deviation = 0.008 Å) with the pyrazine ring being located about a center of symmetry. Both the nitrogen and sulfur potential coordination sites are orientated *exo* to their respective rings.

The molecular structure of ligand **L2** is illustrated in Fig. 2. The molecule also possesses inversion symmetry with the

pyrazine ring being located about a center of symmetry. It consists of two S–CH$_2$–CH$_2$–S chains linked by the central rigid tetra-2,3,5,6-methylenepyrazine unit, forming eight-membered rings. The configuration of these rings fits best to the definition for a twist-boat-chair (Evans & Boeyens, 1988; Spek, 2020), with a pseudo twofold rotation axis bisecting the C1—C2 and C4—C5 bonds and their symmetry equivalents. The molecule is step-shaped with six potential sites for coordination.

I

II

The reaction of **L1** with silver nitrate leads to the formation of a two-dimensional coordination polymer, (**I**), with the
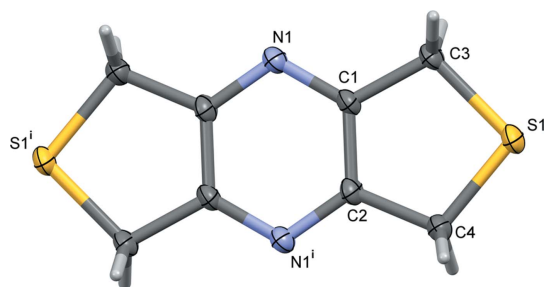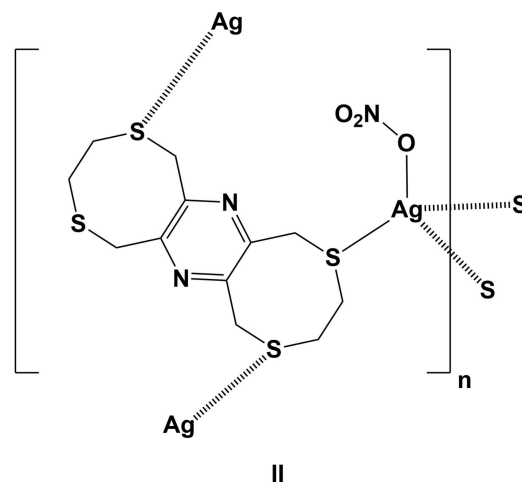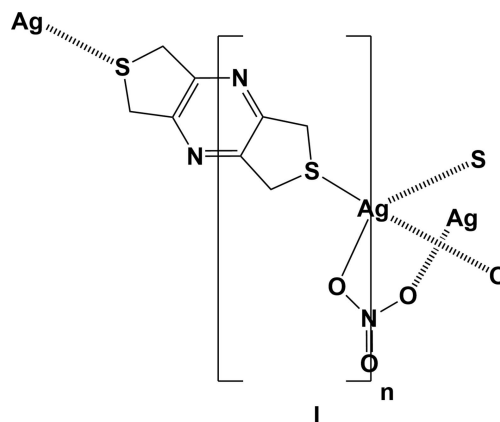

Figure 1
The molecular structure of **L1**, with atom labelling [symmetry code: (i) −*x* + 1, −*y* + 1, −*z* + 1]. Displacement ellipsoids are drawn at the 30% probability level.
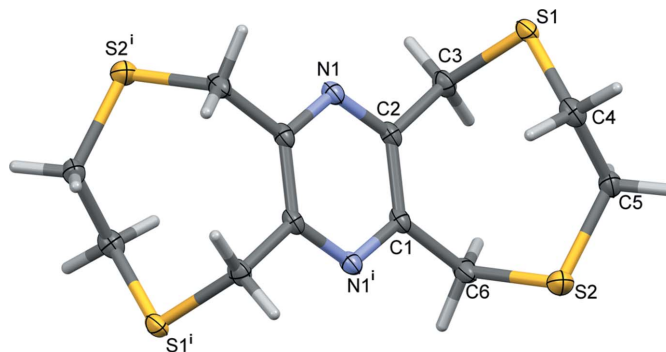

Figure 2
The molecular structure of **L2**, with atom labelling; symmetry code: (i) −*x* + $\frac{3}{2}$, −*y* + $\frac{1}{2}$, −*z* + 1]. Displacement ellipsoids are drawn at the 30% probability level.

Table 1
Selected geometric parameters (Å, °) for **I**.

Ag1—S1	2.4696 (5)	Ag1—O1	2.5849 (15)
S1—Ag1—S1^i	152.57 (2)	S1—Ag1—O1^i	103.30 (3)
S1—Ag1—O1	97.62 (3)	O1—Ag1—O1^i	80.24 (7)

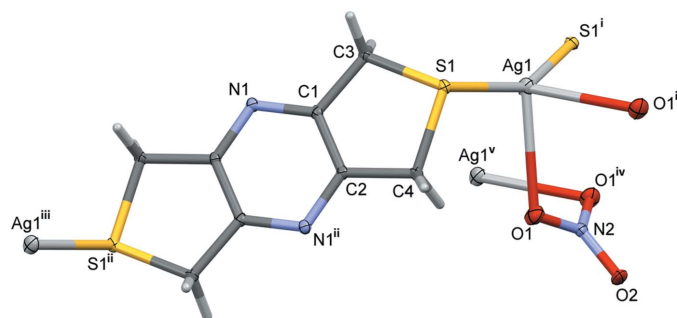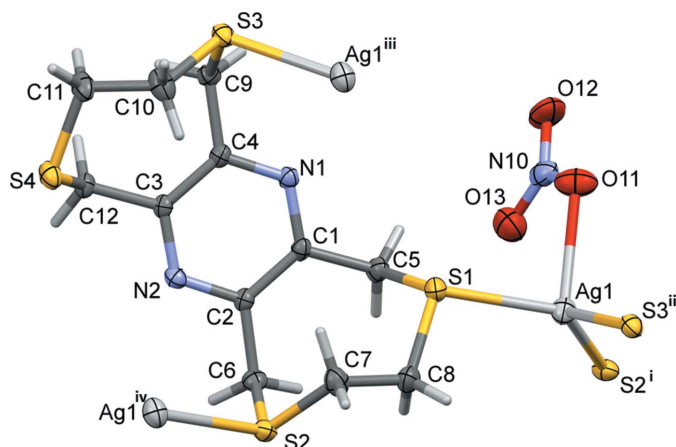Symmetry code: (i) $-x + \frac{1}{2}, y, -z + \frac{3}{2}$.

Table 2
Selected geometric parameters (Å, °) for **II**.

Ag1—S1	2.5927 (10)	Ag1—S3^{ii}	2.5382 (9)
Ag1—S2^i	2.4760 (10)	Ag1—O11	2.492 (3)
S2^i—Ag1—S1	132.51 (3)	O11—Ag1—S1	93.62 (8)
S3^{ii}—Ag1—S1	97.47 (3)	S2^i—Ag1—O11	97.12 (8)
S2^i—Ag1—S3^{ii}	121.65 (3)	O11—Ag1—S3^{ii}	109.25 (8)

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.

nitrato anion bridging two equivalent silver atoms (Fig. 3). Selected bond lengths and bond angles are given in Table 1. The central pyrazine ring is situated about an inversion center and the silver atom Ag1 and atoms N2 and O2 of the nitrato anion lie on a twofold rotation axis. Atom Ag1 has a fourfold AgO$_2$S$_2$ coordination sphere with a distorted shape. The fourfold geometry index τ_4 has a value of 0.74 ($\tau_4 = 1$ for a perfect tetrahedral geometry, 0 for a perfect square-planar geometry and 0.85 for perfect trigonal–pyramidal geometry; Yang *et al.*, 2007). The intermediate value of 0.74 tends towards a see-saw arrangement. This seems reasonable in view of the fact that atom Ag1 is located on a twofold rotation axis.

The reaction of **L2** with silver nitrate also leads to the formation of a two-dimensional coordination polymer (**II**, Fig. 4). Selected bond lengths and bond angles are given in Table 2. While the ligand has a step-shape in the solid state with one eight-membered ring directed above the pyrazine ring and the other below (Fig. 2), in the complex it has a boat shape with both eight-membered rings directed to the same side of the pyrazine ring (Fig. 4). The configuration of these rings again fits best to the definition for a twist-boat-chair (Evans & Boeyens, 1988; Spek, 2020), with a pseudo twofold rotation axis bisecting bonds C1—C2 and C7—C8 and bonds C3—C4 and C10—C11. The nitrato anion coordinates to the

Figure 4
The asymmetric unit of complex **II**, with atom labelling [symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$); (iii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$]. Displacement ellipsoids are drawn at the 30% probability level.

silver atom in a monodentate manner *via* atom O11 (Fig. 4, Table 2). The silver atom Ag1 has a fourfold AgOS$_3$ coordination sphere with a distorted shape. The fourfold geometry index τ_4 has a value of 0.75, which again tends towards a see-saw arrangement.

The pyrazine N atoms are not involved in coordination to the silver atom in either **I** or **II**; the silver atom prefers coordination to the S atoms in both complexes. The role of the nitrato anion in **I** is essential in forming the two-dimensional network, bridging two equivalent silver atoms, while in **II** the nitrato anion coordinates to atom Ag1 in a monodentate manner. There is a significant difference in the Ag—S bond lengths and the Ag—O bond lengths in compounds **I** and **II** (*cf.* Tables 1 and 2), which are discussed in §5. *Database survey.*

3. Supramolecular features

In the crystals of both **L1** and **L2**, there are no significant intermolecular interactions present (Figs. 5 and 6, respectively).

In the crystal of **I**, the coordination networks lie parallel to the *ac* plane (Fig. 7) and are linked by C—H···O hydrogen

Figure 3
The asymmetric unit of complex **I**, with atom labelling [symmetry codes: (i) $-x + \frac{1}{2}, y, -z + \frac{3}{2}$; (ii) $-x + 1, -y, -z + 2$; (iii) $-x + 1, -y + 1, -z + 2$; (iv) $-x + \frac{3}{2}, y, -z + \frac{3}{2}$; (v) $x + 1, y, z$]. Displacement ellipsoids are drawn at the 30% probability level.
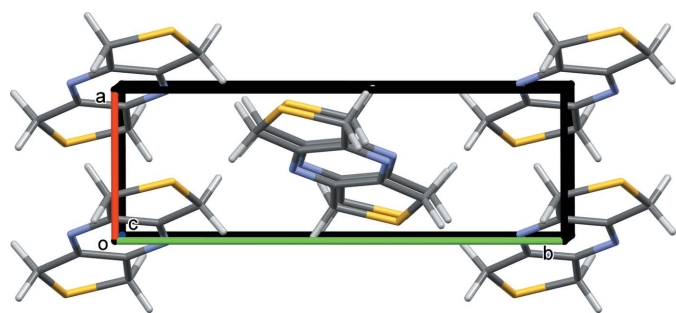
Figure 5
Crystal packing of **L1** viewed along the *c* axis. The molecules stack in columns up the *a* axis.

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$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C3-H3B \cdots O1^{ii}$	0.98	2.50	3.379 (2)	150

Symmetry code: (ii) $x, y - 1, z$.

Table 4
Hydrogen-bond geometry (Å, °) for **II**.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C5-H5A \cdots O13$	0.97	2.51	3.239 (5)	132
$C6-H6A \cdots O12^{iii}$	0.97	2.56	3.442 (5)	150
$C8-H8B \cdots S4^{i}$	0.97	2.74	3.696 (4)	169
$C12-H12B \cdots O12^{iv}$	0.97	2.37	3.177 (4)	140

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x + 1, y, z$; (iv) $-x, -y, -z + 1$.

bonds, forming a supramolecular framework (Fig. 8 and Table 3).

In the crystal of **II**, the coordination networks lie parallel to the *ab* plane (Fig. 9). They are linked by C—H⋯O and C—H⋯S hydrogen bonds, forming a supramolecular framework (Fig. 10 and Table 4).

Figure 8
A view along the *a* axis of the crystal packing of complex **I**. The hydrogen bonds are shown as dashed lines (Table 3).
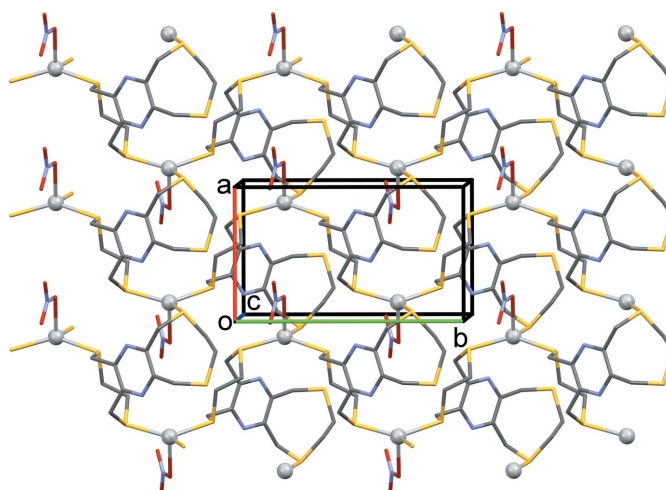
Figure 9
A view along the *c* axis of the crystal packing of complex **II**, illustrating the formation of the metal–organic network. The silver atoms are shown as grey balls. For clarity, the H atoms have been omitted.

Figure 6
Crystal packing of **L2** viewed along the *b* axis. The molecules stack in columns up the *c* axis.

Figure 7
A view along the *b* axis of the crystal packing of complex **I**, illustrating the formation of the metal–organic network. The silver atoms are shown as grey balls.

Figure 10
A view along the *a* axis of the crystal packing of complex **II**. The hydrogen bonds are shown as dashed lines (Table 4). For clarity, only the H atoms involved in these interactions have been included.

Table 5
Short interatomic contacts^a (Å) in **L1** and **L2**.

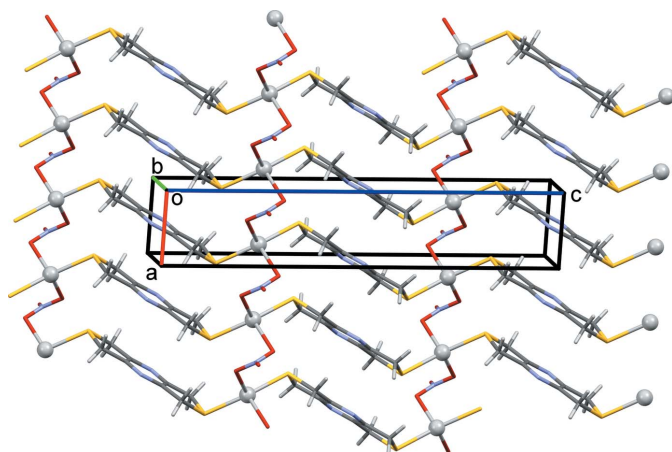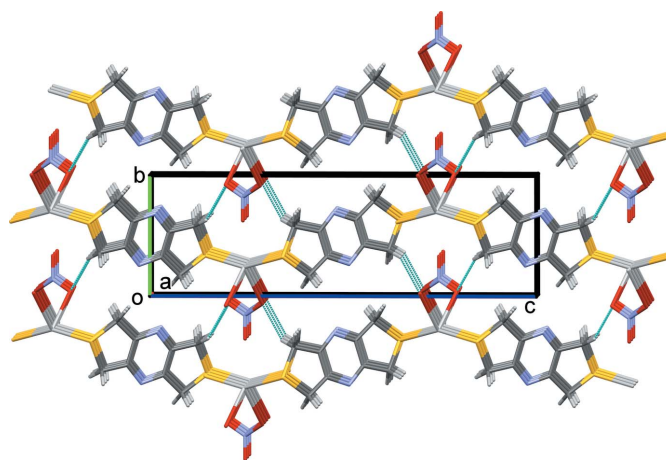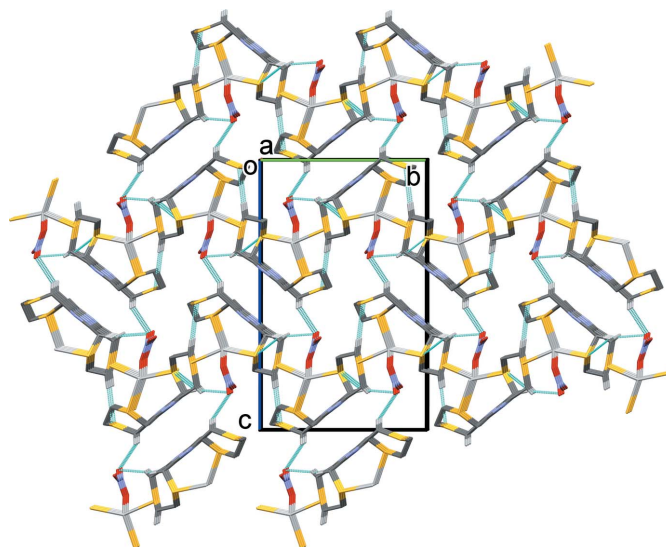| Atom 1	Atom 2	Length	Length − vdW	Symm. op. 1	Symm. op. 2
L1					
H3A	H3A	2.313	−0.087	$1 - x, 1 - y, -z$	$x, y, -1 + z$
H3B	C1	2.876	−0.024	x, y, z	$-1 + x, y, z$
S1	H3A	3.000	0.000	$1 - x, 1 - y, -z$	$x, y, -1 + z$
H3B	N1	2.757	0.007	x, y, z	$-1 + x, y, z$
S1	C3	3.515	0.015	x, y, z	$-x, 1 - y, 1 - z$
N1	S1	3.379	0.029	x, y, z	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
S1	C2	3.537	0.037	x, y, z	$-1 + x, y, z$
H3B	H4B	2.452	0.052	x, y, z	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
C3	H3A	2.998	0.098	$1 - x, 1 - y, -z$	$x, y, -1 + z$
L2					
H6B	C2	2.699	−0.201	x, y, z	$\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
S1	H6A	2.919	−0.081	$\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$	$\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
S1	H5A	2.992	−0.008	$\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$	$-\frac{1}{2} + x, -\frac{1}{2} + y, z$
S2	H4B	3.017	0.017	x, y, z	$x, -y, -\frac{1}{2} + z$
S1	C5	3.525	0.025	$\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$	$-\frac{1}{2} + x, -\frac{1}{2} + y, z$

Note: (a) Calculated using *Mercury* (Macrae *et al.*, 2020).

4. Hirshfeld surface analysis and two-dimensional fingerprint plots

The Hirshfeld surface (HS) analyses (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were performed with *Crystal-Explorer17* (Turner *et al.*, 2017) following the protocol of Tiekink and collaborators (Tan *et al.*, 2019). A summary of the short interatomic contacts in **L1** and **L2** is given in Table 5.

The Hirshfeld surfaces of **L1** and **L2** mapped over d_{norm} are given in Fig. 11a and b, respectively. They show that there are no short significant interatomic contacts present in the crystal of **L1**, while the red spots indicate that short contacts are significant in the crystal of **L2**.

The full two-dimensional fingerprint plots for **L1** and **L2** are given in Figs. 12 and 13, respectively. The principal intermolecular interactions for **L1** are delineated into the following contacts: H···H at 41.7%, S···H/H···S at 25.3%, N···H/H···N at 17.1%, C···H/H···C at 6.5% and N···S at 3.7%. For **L2**, the principal intermolecular interactions are delineated into H···H contacts at 45.2%, S···H/H···S at 36.6%, N···H/H···N at 11.7%, C···H/H···C at 4.7% and S···S at 1.8%. The S···H/H···S contacts, with the sharp spikes at $d_{\text{e}} + d_{\text{i}} \simeq 2.9$ Å in Fig. 12c for **L1** and at $\simeq 2.80$ Å in Fig. 13c for **L2**, make significant contributions, especially for **L2**, which corresponds to the indications given in Fig. 11b, the HS of **L2** mapped over d_{norm}, and in Table 5. In Fig. 13e the sharp spikes at $d_{\text{e}} + d_{\text{i}} \simeq 2.6$ Å indicate the significant contribution of the C···H/H···C contacts in the crystal of **L2**.

Figure 12
The full two-dimensional fingerprint plot for **L1**, and fingerprint plots delineated into H···H, S···H/H···S, N···H/H···N, C···H/H···C, and N···S contacts.

Figure 13
The full two-dimensional fingerprint plot for **L2**, and fingerprint plots delineated into H···H, S···H/H···S, N···H/H···N, C···H/H···C, and S···S contacts.
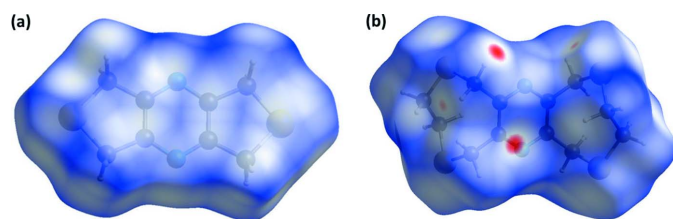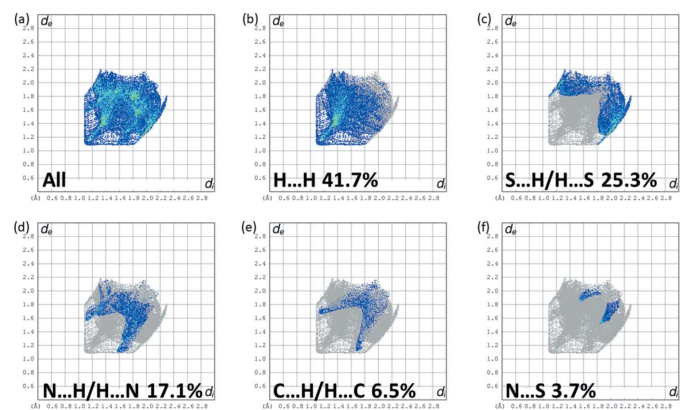

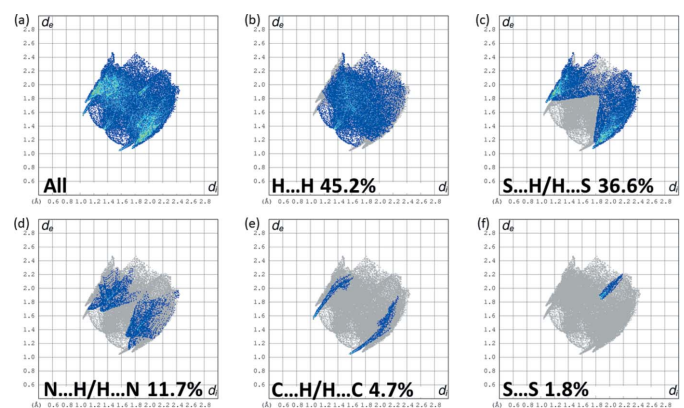**Figure 11**
(a) The Hirshfeld surface of **L1**, mapped over d_{norm} in the colour range 0.0058 to 0.9525 a.u. and (b) the Hirshfeld surface of compound **L2**, mapped over d_{norm} in the colour range −0.1279 to 1.1192 a.u..

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.41, last update November 2019; Groom *et al.*, 2016) for the benzene analogue of **L1**, *i.e.* 5,7-dihydro-1*H*,3*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene, gave ten hits. Five compounds concern silver(I) coordination complexes involving various anions, *viz. catena*-[[μ_2-5,7-dihydro-1*H*,3*H*-thieneo(3,4-*f*)(2)-benzothiophene]bis(acetonitrile)silver(I) hexafluoridophosphate] (MIZHAE; Melcer *et al.*, 2001), *catena*-[[μ_3-1,2:4,5-dithiolo(*c*)benzene-*S,S,S'*]bis(acetonitrile)silver(I) tetrafluoridoborate] (NUTBUZ; Shimizu *et al.*, 1998], *catena*-[[μ_3-1,2:4,5-dithiolo(*c*)benzene-*S,S,S'*]benzonitrilosilver tetrafluoridoborate benzonitrile solvate] (NUTCAG; Shimizu *et al.*, 1998)], *catena*-[[μ_3-benzene-1,2:4,5-bis(3',4'-thiolane)](*p*-tolylsulfonato)silver(I) benzene clathrate] (QACYUO; Shimizu *et al.*, 1999) and *catena*-[bis(μ_2-5,7-dihydro-1*H*,3*H*-thieno(3,4-*f*)(2)benzothiophene)bis(*p*-tosyloxy)disilver(I) benzene solvate] (QACYUO01; Melcer *et al.*, 2001). The latter are two reports of the same compound, *cf*. unit-cell parameters and space group.

The compound MIZHAE is a three-dimensional coordination polymer with a fourfold geometry index τ_4 value of 0.80 (close to a trigonal–pyramidal geometry) for the silver atom, which has an AgN_2S_2 coordination sphere. NUTBUZ is a two-dimensional coordination polymer. Here, the silver atom has a fivefold AgN_2S_3 coordination sphere with a distorted shape; the fivefold geometry index τ_5 is 0.77 ($\tau_5 = 1$ for perfect trigonal–pyramidal geometry and $= 0$ for perfect square-pyramidal geometry; Addison *et al.*, 1984). NUTCAG is a two-dimensional coordination polymer with a τ_4 value of 0.73 for the silver atom, which has an $AgNS_3$ coordination sphere. QACYUO (and QACYUO0) is a two-dimensional coordination polymer, with the silver atom having a fourfold $AgOS_3$ coordination sphere with a trigonal–pyramidal geometry, the fourfold geometry index τ_4 being 0.83. The Ag—S bond lengths involving the fourfold coordinated silver atoms vary from 2.4708 (13) Å in NUTCAG to 2.6077 (7) Å in QACYUO/01. The values of the various Ag—S bond lengths in **I** and **II** fall within these limits (see Tables 1 and 2). While in the ligand **L1** the five-membered thiophene rings are planar, in the above mentioned structures and in complex **I** they have envelope configurations with the S atom as the flap.

The nitrate anion can coordinate in at least ten different ways and is extremely useful for designing multi-dimensional coordination polymers, as shown by a search of the CSD. We have previously examined the role of the nitrate anion in the formation of coordination polymers when reporting on the results of the reaction of silver nitrate with some tetrakis-thioether-substituted pyrazine ligands (Assoumatine & Stoeckli-Evans, 2017). For the two-dimensional coordination polymer (CSD refcode XALPOS) poly[di-μ-nitrato-bis{μ-2,3,5,6-tetrakis[(phenylsulfanyl)methyl]pyrazine}disilver(I)] the Ag—O bond lengths vary from 2.507 (4) to 2.551 (4) Å. For the three-dimensional coordination polymer (XALPUY) poly[trinitrato{μ_6-2,3,5,6-tetrakis[(pyridin-2-ylsulfanyl)methyl]pyrazine}trisilver(I)], the Ag—O bond lengths vary from

2.567 (5) to 2.752 (5) Å. The values observed for **I** and **II**, 2.5849 (15) and 2.492 (3) Å, respectively, are similar to those mentioned above.

A search of the CSD for the benzene analogue of **L2**, or complexes of this analogue, gave zero hits.

6. Synthesis and crystallization

The reagent tetra-2,3,5,6-bromomethyl-pyrazine (**TBr**) was first synthesized by Ferigo *et al.* (1994), and its crystal structure has been reported (CSD refcode: TOJXUN; Assoumatine & Stoeckli-Evans, 2014). The IR spectra for ligands **L1** and **L2**, and for complexes **I** and **II**, are given in Fig. S1 in the supporting information.

Synthesis of 5,7-dihydro-1*H*,3*H*-dithieno[3,4-*b*:3',4'-*e*]pyrazine (L1):

Ligand **L1** was first prepared by the reaction of **TBr** with $Na_2S\cdot9H_2O$, using the procedure of Shimizu *et al.* (1998). This gave a crude brown solid, which was chromatographed on deactivated silica gel with CH_2Cl_2 as eluent to yield 35% of a white solid.

The yield could be increased by as much as 11% using a method similar to that described by Boekelheide *et al.* (1973). Well-ground $Na_2S\cdot9H_2O$ (1.06 g, 4.42 mmol, Aldrich 99%) was dissolved in a solution of $MeOH/CH_2Cl_2$ (100 ml, 1/1 *v/v*) in a three-necked flask (500 ml) equipped with a reflux condenser topped by a $CaCl_2$ drying tube, an addition funnel (50 ml) and a magnetic stirring bar. To this mixture was added slowly through the addition funnel a solution of **TBr** (1 g, 2.21 mmol) in CH_2Cl_2 (25 ml). The reaction mixture was stirred vigorously for 3 h. Removal of the solvent resulted in a brown residue that was extracted into CH_2Cl_2 (200 ml), washed with water (3 × 30 ml), dried over anhydrous MgSO4 and then, after filtration, evaporated to dryness. The resultant residue was chromatographed over deactivated silica gel using CH_2Cl_2 as eluent. The main eluted fraction was evaporated to give a white solid that was dried under vacuum yielding pure **L1** (m.p. 518–521 K, with decomposition). Colourless rod-like crystals were formed from a concentrated solution of pure **L1** in CH_2Cl_2, after standing for one week at 278 K.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.22 (*s*, 8H, Pz–CH_2–S) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.30, 34.44 ppm. Analysis for $C_8H_8N_2S_2$ ($M_r = 196.30$ g mol^{-1}). Calculated (%): C 48.95, H 4.11, N 14.27, S 32.67. Found (%): C 49.02, H 4.23, N 14.04, S 32.60. MS (EI, 70 eV), *m/z* (%): 196 ([M^+], 100).

Synthesis of 3,4,8,10,11,13-hexahydro-1*H*,6*H*-bis([1,4]dithiocino)[6,7-*b*:6',7'-*e*]pyrazine (L2):

A 500 ml three-necked flask was equipped with a reflux condenser, a 50 ml addition funnel, and a magnetic stirring bar. The entire system was purged and kept under a nitrogen atmosphere using vacuum line techniques. Then well-ground Cs_2CO_3 (3.52 g, 10.80 mmol, Fluka 99%) was suspended in DMF (250 ml) in the flask. To this well-stirred suspension was added dropwise through the addition funnel a solution of **TBr** (1 g, 2.21 mmol) and 1,2-ethanedithiol (0.4 ml, 4.76 mmol, 98%) dissolved in DMF (50 ml), at a rate of about 10 ml h^{-1}. The mixture was stirred for a further 20 h and then filtered.

Table 6
Experimental details.

	L1	L2	I	II
Crystal data				
Chemical formula	$[Ag(NO_3)(C_8H_8N_2S_2)]$	$[Ag(NO_3)(C_{12}H_{16}N_2S_4)]$	$[C_8H_8N_2S_2]AgNO_3$	$[C_{12}H_{16}N_2S_4]AgNO_3$
M_r	196.28	316.51	366.16	486.39
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $C2/c$	Monoclinic, $P2/n$	Monoclinic, $P2_1/c$
Temperature (K)	223	223	223	293
a, b, c (Å)	4.1027 (4), 12.1789 (18), 8.1014 (8)	21.1618 (18), 7.0585 (5), 9.5057 (7)	3.8995 (3), 6.3902 (6), 20.5741 (18)	7.0777 (6), 12.0654 (7), 19.5725 (18)
β (°)	95.780 (12)	94.47 (1)	93.121 (9)	90.446 (10)
V (Å^3)	402.74 (8)	1415.55 (19)	511.92 (8)	1671.3 (2)
Z	2	4	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.60	0.65	2.37	1.72
Crystal size (mm)	$0.45 \times 0.13 \times 0.10$	$0.40 \times 0.30 \times 0.10$	$0.45 \times 0.10 \times 0.10$	$0.50 \times 0.23 \times 0.08$
Data collection				
Diffractometer	STOE IPDS 1	STOE IPDS 1	STOE IPDS 1	STOE IPDS 1
Absorption correction	–	–	Multi-scan (*MULABS*; Spek, 2020)	Multi-scan (*MULABS*; Spek, 2020)
T_{min}, T_{max}	–	–	0.932, 1.000	0.939, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3025, 744, 590	5086, 1367, 1174	3795, 958, 905	12808, 3222, 2226
R_{int}	0.159	0.029	0.021	0.051
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.611	0.615	0.613	0.614
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.074, 0.180, 1.03	0.026, 0.071, 1.05	0.016, 0.041, 1.15	0.029, 0.059, 0.85
No. of reflections	744	1367	958	3222
No. of parameters	55	82	79	208
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.77, −0.55	0.31, −0.25	0.31, −0.27	0.61, −0.42

Computer programs: *EXPOSE*, *CELL* and *INTEGRATE* in *IPDS1* (Stoe & Cie, 1998), *SHELXS97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2020), *SHELXL2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

The orange filtrate was evaporated under reduced pressure. The residue was extracted into CH_2Cl_2 (300 ml) then washed with water (3 × 30 ml), dried over anhydrous $MgSO_4$ and then, after filtration, evaporated to dryness. The resultant residue was chromatographed over deactivated silica gel using CH_2Cl_2 as eluent. The main eluted fraction was evaporated to give a white solid that was dried under vacuum to obtain 0.35 g (50% yield) of pure **L2** (m.p. 541–544 K, with decomposition). Slow evaporation at room temperature of a solution of **L2** in $CHCl_3$ in a 5 mm diameter glass tube gave colourless plate-like crystals.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.08 (s, 8H, Pz–CH$_2$–S), 2.92 (s, 8H, S–CH$_2$–CH$_2$–S) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 151.15, 34.40, 34.09 ppm. Analysis for $C_{12}H_{16}N_2S_4$ (M_r = 316.54 g mol^{-1}). Calculated (%): C 45.53, H 5.09, N 8.85, S 40.52. Found (%): C 45.34, H 5.30, N 8.68, S 40.33. MS (EI, 70 eV), m/z (%): 316 ([M^+], 98.7).

Synthesis of complex I:

A solution of **L1** (15 mg, 0.08 mmol) in THF (5 ml) was introduced into a 16 mm diameter glass tube and layered with MeCN (2 ml) as a buffer zone. Then a solution of AgNO$_3$ (14 mg, 0.08 mmol) in MeCN (5 ml) was added very gently to avoid possible mixing. The glass tube was sealed and left in the dark at room temperature for at least two weeks, whereupon colourless needle-like crystals of complex **I** were isolated in the buffer zone.

Analysis for $C_8H_8N_3O_3S_2Ag$ (M_r = 366.18 g mol^{-1}). Calculated (%): C 26.24, H 2.21, N 11.48, S 17.51. Found (%): C 26.27, H 2.10, N 11.29, S 17.19.

Synthesis of complex II:

A solution of **L2** (20 mg, 0.06 mmol) in CH_2Cl_2 (10 ml) was introduced into a 16 mm diameter glass tube and layered with MeCN (2 ml) as a buffer zone. Then a solution of AgNO$_3$ (10 mg, 0.06 mmol) in MeCN (5 ml) was added very gently to avoid possible mixing. The glass tube was sealed and left in the dark at room temperature for at least three weeks, whereupon thin, colourless plate-like crystals of complex **II** were isolated at the interface between the two solutions. No analytical data are available for this complex.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 6. The C-bound H atoms were included in calculated positions and treated as riding on the parent atoms: C—H = 0.97–0.98 Å with U_{iso}(H) = 1.2U_{eq}(C). For **L1**, the rather high R_{int} value of 0.159 is due to the poor quality, *viz*. large mosaic spread, of the crystal.

Acknowledgements

research communications

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supporting information

Silver(I) nitrate two-dimensional coordination polymers of two new pyrazine-thiophane ligands: 5,7-dihydro-1*H*,3*H*-dithieno[3,4-*b*:3′,4′-*e*]pyrazine and 3,4,8,10,11,13-hexahydro-1*H*,6*H*-bis([1,4]dithiocino)[6,7-*b*:6′,7′-*e*]pyrazine

Tokouré Assoumatine and Helen Stoeckli-Evans

Computing details

For all structures, data collection: *EXPOSE* in *IPDS1* (Stoe & Cie, 1998); cell refinement: *CELL* in *IPDS1* (Stoe & Cie, 1998); data reduction: *INTEGRATE* in *IPDS1* (Stoe & Cie, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL-2018/3* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *SHELXL-2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

Poly[(*μ*-5,7-dihydro-1*H*,3*H*-dithieno[3,4-*b*;3′,4′-*e*]pyrazine-*κ*²*S*:*S*′)(*μ*-nitrato-*κ*²*O*:*O*′)silver(I)] (L1)

Crystal data

$[Ag(NO_3)(C_8H_8N_2S_2)]$	$F(000) = 204$
$M_r = 196.28$	$D_x = 1.619$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.1027$ (4) Å	Cell parameters from 3541 reflections
$b = 12.1789$ (18) Å	$\theta = 3.1$–$25.7°$
$c = 8.1014$ (8) Å	$\mu = 0.60$ mm^{-1}
$\beta = 95.780$ (12)°	$T = 223$ K
$V = 402.74$ (8) Å^3	Rod, colourless
$Z = 2$	$0.45 \times 0.13 \times 0.10$ mm

Data collection

STOE IPDS 1 diffractometer	590 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.159$
Plane graphite monochromator	$\theta_{max} = 25.8°$, $\theta_{min} = 3.0°$
φ rotation scans	$h = -4 \rightarrow 4$
3025 measured reflections	$k = -14 \rightarrow 14$
744 independent reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.074$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.180$	
$S = 1.03$	Hydrogen site location: inferred from neighbouring sites
744 reflections	
55 parameters	H-atom parameters constrained
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.1296P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.1126 (2)	0.62437 (7)	0.34804 (9)	0.0363 (5)
N1	0.4717 (8)	0.3945 (2)	0.0713 (4)	0.0320 (7)
C1	0.3670 (8)	0.4860 (3)	0.1411 (3)	0.0296 (9)
C2	0.3971 (9)	0.5902 (3)	0.0708 (4)	0.0303 (8)
C3	0.2147 (9)	0.4824 (3)	0.3009 (3)	0.0341 (9)
H3A	0.368695	0.451919	0.389472	0.041*
H3B	0.016898	0.436835	0.289632	0.041*
C4	0.2721 (10)	0.6844 (3)	0.1673 (4)	0.0356 (9)
H4A	0.098963	0.724060	0.099563	0.043*
H4B	0.450057	0.735867	0.201262	0.043*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0477 (8)	0.0408 (6)	0.0219 (6)	0.0041 (3)	0.0106 (4)	−0.0011 (3)
N1	0.0412 (18)	0.0333 (14)	0.0219 (15)	0.0007 (11)	0.0049 (11)	0.0019 (10)
C1	0.034 (2)	0.0354 (18)	0.0197 (17)	−0.0011 (12)	0.0062 (13)	0.0012 (11)
C2	0.039 (2)	0.0349 (17)	0.0161 (15)	0.0014 (14)	0.0007 (12)	−0.0031 (12)
C3	0.048 (2)	0.0363 (17)	0.0187 (18)	0.0023 (14)	0.0061 (15)	0.0031 (12)
C4	0.048 (2)	0.0328 (17)	0.0268 (16)	0.0012 (14)	0.0096 (15)	0.0010 (12)

Geometric parameters (Å, º)

S1—C4	1.817 (4)	C2—C4	1.507 (5)
S1—C3	1.828 (3)	C3—H3A	0.9800
N1—C2^i	1.332 (4)	C3—H3B	0.9800
N1—C1	1.340 (4)	C4—H4A	0.9800
C1—C2	1.401 (5)	C4—H4B	0.9800
C1—C3	1.494 (4)		
C4—S1—C3	95.95 (14)	S1—C3—H3A	110.5
C2^i—N1—C1	115.0 (3)	C1—C3—H3B	110.5
N1—C1—C2	122.5 (3)	S1—C3—H3B	110.5
N1—C1—C3	121.4 (3)	H3A—C3—H3B	108.7
C2—C1—C3	116.1 (3)	C2—C4—S1	106.3 (2)
N1^i—C2—C1	122.5 (3)	C2—C4—H4A	110.5

N1^{i}—C2—C4	122.0 (3)	S1—C4—H4A	110.5
C1—C2—C4	115.5 (3)	C2—C4—H4B	110.5
C1—C3—S1	106.1 (2)	S1—C4—H4B	110.5
C1—C3—H3A	110.5	H4A—C4—H4B	108.7
C2^{i}—N1—C1—C2	−0.8 (5)	N1—C1—C3—S1	179.8 (3)
C2^{i}—N1—C1—C3	−179.9 (3)	C2—C1—C3—S1	0.7 (4)
N1—C1—C2—N1^{i}	0.8 (6)	C4—S1—C3—C1	−1.1 (3)
C3—C1—C2—N1^{i}	180.0 (3)	N1^{i}—C2—C4—S1	179.2 (3)
N1—C1—C2—C4	−178.9 (3)	C1—C2—C4—S1	−1.0 (4)
C3—C1—C2—C4	0.3 (5)	C3—S1—C4—C2	1.2 (3)

Symmetry code: (i) −x+1, −y+1, −z.

Poly[[$\mu_3$3,4,8,10,11,13-hexahydro-1H,6H-bis([1,4]dithiocino)[6,7-b;6′,7′-e]pyrazine-$\kappa^3 S$:S':S''](nitrato-κO)silver(I)] (L2)

Crystal data

[Ag(NO$_3$)(C$_{12}$H$_{16}$N$_2$S$_4$)]	$F(000) = 664$
$M_r = 316.51$	$D_x = 1.485$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 21.1618$ (18) Å	Cell parameters from 5000 reflections
$b = 7.0585$ (5) Å	$\theta = 3.0$–25.9°
$c = 9.5057$ (7) Å	$\mu = 0.65$ mm^{-1}
$\beta = 94.47$ (1)°	$T = 223$ K
$V = 1415.55$ (19) Å^3	Colourless, plate
$Z = 4$	$0.40 \times 0.30 \times 0.10$ mm

Data collection

STOE IPDS 1 diffractometer	1174 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.029$
Plane graphite monochromator	$\theta_{max} = 25.9°$, $\theta_{min} = 3.0°$
φ rotation scans	$h = -25 \rightarrow 25$
5086 measured reflections	$k = -8 \rightarrow 8$
1367 independent reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.026$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.071$	
$S = 1.05$	H-atom parameters constrained
1367 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.461P]$ where $P = (F_o^2 + 2F_c^2)/3$
82 parameters	
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.31$ e Å^{-3}
	$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.90795 (2)	0.54315 (6)	0.52645 (5)	0.03312 (15)
S2	0.89795 (2)	0.01187 (6)	0.34452 (5)	0.03987 (16)
N1	0.75497 (6)	0.42931 (19)	0.55990 (14)	0.0268 (3)
C1	0.78592 (7)	0.1989 (2)	0.39521 (15)	0.0253 (3)
C2	0.79056 (6)	0.3798 (2)	0.45558 (15)	0.0246 (3)
C3	0.83585 (8)	0.5281 (2)	0.41003 (18)	0.0303 (4)
H3A	0.814637	0.651638	0.407231	0.036*
H3B	0.847038	0.498872	0.314291	0.036*
C4	0.93325 (8)	0.2996 (2)	0.54130 (17)	0.0323 (4)
H4A	0.970847	0.293157	0.608187	0.039*
H4B	0.899694	0.225955	0.581154	0.039*
C5	0.94907 (7)	0.2061 (2)	0.40278 (18)	0.0319 (4)
H5A	0.992794	0.159497	0.414165	0.038*
H5B	0.947061	0.302840	0.328648	0.038*
C6	0.82558 (7)	0.1326 (3)	0.27995 (17)	0.0332 (4)
H6A	0.836729	0.242364	0.223784	0.040*
H6B	0.800162	0.046620	0.217500	0.040*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0246 (2)	0.0341 (2)	0.0413 (3)	−0.01170 (15)	0.00595 (17)	−0.01108 (17)
S2	0.0336 (3)	0.0307 (2)	0.0562 (3)	−0.00329 (16)	0.0090 (2)	−0.01143 (19)
N1	0.0215 (6)	0.0287 (7)	0.0300 (7)	−0.0059 (5)	0.0004 (5)	−0.0012 (5)
C1	0.0196 (7)	0.0326 (8)	0.0231 (8)	−0.0055 (6)	−0.0017 (6)	0.0008 (6)
C2	0.0186 (7)	0.0295 (8)	0.0252 (8)	−0.0058 (6)	−0.0013 (6)	0.0032 (6)
C3	0.0266 (8)	0.0289 (8)	0.0356 (9)	−0.0071 (6)	0.0044 (6)	0.0035 (7)
C4	0.0292 (8)	0.0375 (9)	0.0296 (8)	−0.0063 (7)	−0.0008 (6)	0.0047 (7)
C5	0.0226 (7)	0.0330 (8)	0.0402 (9)	−0.0016 (6)	0.0039 (6)	−0.0010 (7)
C6	0.0281 (8)	0.0435 (9)	0.0283 (8)	−0.0109 (7)	0.0038 (6)	−0.0085 (7)

Geometric parameters (Å, º)

S1—C4	1.8025 (17)	C3—H3A	0.9800
S1—C3	1.8168 (17)	C3—H3B	0.9800
S2—C5	1.8062 (16)	C4—C5	1.533 (2)
S2—C6	1.8171 (18)	C4—H4A	0.9800
N1—C2	1.338 (2)	C4—H4B	0.9800
N1—C1[i]	1.3443 (19)	C5—H5A	0.9800

C1—C2	1.401 (2)	C5—H5B	0.9800
C1—C6	1.506 (2)	C6—H6A	0.9800
C2—C3	1.506 (2)	C6—H6B	0.9800
C4—S1—C3	102.85 (8)	S1—C4—H4A	108.5
C5—S2—C6	102.50 (8)	C5—C4—H4B	108.5
C2—N1—C1^i	118.24 (14)	S1—C4—H4B	108.5
N1^i—C1—C2	120.67 (14)	H4A—C4—H4B	107.5
N1^i—C1—C6	115.54 (14)	C4—C5—S2	115.13 (11)
C2—C1—C6	123.79 (13)	C4—C5—H5A	108.5
N1—C2—C1	121.09 (13)	S2—C5—H5A	108.5
N1—C2—C3	116.07 (14)	C4—C5—H5B	108.5
C1—C2—C3	122.83 (14)	S2—C5—H5B	108.5
C2—C3—S1	112.86 (11)	H5A—C5—H5B	107.5
C2—C3—H3A	109.0	C1—C6—S2	113.75 (11)
S1—C3—H3A	109.0	C1—C6—H6A	108.8
C2—C3—H3B	109.0	S2—C6—H6A	108.8
S1—C3—H3B	109.0	C1—C6—H6B	108.8
H3A—C3—H3B	107.8	S2—C6—H6B	108.8
C5—C4—S1	115.28 (11)	H6A—C6—H6B	107.7
C5—C4—H4A	108.5		
C1^i—N1—C2—C1	−0.5 (2)	C4—S1—C3—C2	49.78 (13)
C1^i—N1—C2—C3	−179.60 (14)	C3—S1—C4—C5	61.99 (13)
N1^i—C1—C2—N1	0.6 (2)	S1—C4—C5—S2	−115.40 (11)
C6—C1—C2—N1	−178.56 (14)	C6—S2—C5—C4	74.34 (13)
N1^i—C1—C2—C3	179.55 (14)	N1^i—C1—C6—S2	−86.52 (14)
C6—C1—C2—C3	0.4 (2)	C2—C1—C6—S2	92.63 (17)
N1—C2—C3—S1	80.06 (15)	C5—S2—C6—C1	−77.62 (13)
C1—C2—C3—S1	−98.99 (15)		

Symmetry code: (i) −x+3/2, −y+1/2, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4B···S2^{ii}	0.98	3.02	3.7465 (17)	132
C5—H5A···S1^{iii}	0.98	2.99	3.5248 (16)	115
C6—H6A···S1^{iv}	0.98	2.92	3.8389 (18)	157

Symmetry codes: (ii) x, −y, z+1/2; (iii) −x+2, −y+1, −z+1; (iv) x, −y+1, z−1/2.

(I)

Crystal data

[$C_8H_8N_2S_2$]AgNO$_3$	c = 20.5741 (18) Å
M_r = 366.16	β = 93.121 (9)°
Monoclinic, $P2/n$	V = 511.92 (8) Å³
a = 3.8995 (3) Å	Z = 2
b = 6.3902 (6) Å	$F(000)$ = 360

$D_x = 2.375$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5000 reflections

$\theta = 3.2–25.8°$

$\mu = 2.37$ mm^{-1}

$T = 223$ K

Needle, colourless

$0.45 \times 0.10 \times 0.10$ mm

Data collection

STOE IPDS 1
    diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

φ rotation scans

Absorption correction: multi-scan
    (MULABS; Spek, 2020)

$T_{min} = 0.932$, $T_{max} = 1.000$

3795 measured reflections

958 independent reflections

905 reflections with $I > 2\sigma(I)$

$R_{int} = 0.021$

$\theta_{max} = 25.8°$, $\theta_{min} = 3.2°$

$h = -4 \rightarrow 4$

$k = -7 \rightarrow 7$

$l = -25 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.016$

$wR(F^2) = 0.041$

$S = 1.15$

958 reflections

79 parameters

0 restraints

Primary atom site location: structure-invariant
    direct methods

Secondary atom site location: difference Fourier
    map

Hydrogen site location: inferred from
    neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.020P)^2 + 0.3928P]$
    where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.31$ e Å^{-3}

$\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Ag1	0.250000	0.73580 (3)	0.750000	0.02211 (9)
S1	−0.02263 (12)	0.64417 (7)	0.85176 (2)	0.01302 (12)
O1	0.6178 (4)	1.0451 (2)	0.79516 (7)	0.0274 (3)
O2	0.750000	1.3371 (3)	0.750000	0.0262 (5)
N1	0.4947 (4)	0.2874 (2)	0.97975 (7)	0.0136 (3)
N2	0.750000	1.1423 (3)	0.750000	0.0157 (5)
C1	0.3461 (5)	0.4408 (3)	0.94406 (8)	0.0126 (4)
C2	0.3516 (5)	0.6499 (3)	0.96379 (8)	0.0124 (4)
C3	0.1666 (5)	0.3949 (3)	0.87926 (9)	0.0143 (4)
H3A	−0.012208	0.288847	0.883653	0.017*
H3B	0.330073	0.344062	0.848344	0.017*
C4	0.1801 (5)	0.8040 (3)	0.91737 (9)	0.0148 (4)
H4A	0.349176	0.899858	0.900192	0.018*
H4B	0.007436	0.886025	0.939085	0.018*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.03440 (16)	0.01965 (13)	0.01297 (13)	0.000	0.00761 (9)	0.000
S1	0.0137 (2)	0.0144 (2)	0.0109 (2)	0.00041 (16)	−0.00013 (16)	0.00061 (15)
O1	0.0383 (9)	0.0218 (7)	0.0230 (7)	−0.0058 (7)	0.0090 (7)	0.0021 (6)
O2	0.0451 (14)	0.0098 (9)	0.0228 (10)	0.000	−0.0058 (9)	0.000
N1	0.0155 (8)	0.0134 (7)	0.0118 (7)	−0.0009 (6)	0.0015 (6)	0.0001 (6)
N2	0.0175 (12)	0.0146 (11)	0.0144 (11)	0.000	−0.0040 (9)	0.000
C1	0.0127 (9)	0.0145 (9)	0.0106 (8)	−0.0012 (7)	0.0021 (6)	0.0009 (7)
C2	0.0136 (9)	0.0134 (9)	0.0104 (8)	−0.0005 (7)	0.0020 (7)	0.0005 (7)
C3	0.0175 (9)	0.0125 (8)	0.0126 (8)	0.0007 (7)	−0.0014 (7)	−0.0010 (7)
C4	0.0198 (10)	0.0128 (8)	0.0114 (8)	0.0006 (7)	−0.0015 (7)	−0.0013 (7)

Geometric parameters (Å, º)

Ag1—S1	2.4696 (5)	N1—C2ⁱⁱ	1.339 (2)
Ag1—S1ⁱ	2.4696 (5)	C1—C2	1.397 (3)
Ag1—O1	2.5849 (15)	C1—C3	1.501 (2)
Ag1—O1ⁱ	2.5849 (15)	C2—C4	1.503 (3)
S1—C3	1.8322 (19)	C3—H3A	0.9800
S1—C4	1.8368 (19)	C3—H3B	0.9800
O1—N2	1.2517 (18)	C4—H4A	0.9800
O2—N2	1.245 (3)	C4—H4B	0.9800
N1—C1	1.337 (2)		
S1—Ag1—S1ⁱ	152.57 (2)	C2—C1—C3	116.38 (16)
S1—Ag1—O1	97.62 (3)	N1ⁱⁱ—C2—C1	122.49 (17)
S1ⁱ—Ag1—O1	103.30 (4)	N1ⁱⁱ—C2—C4	121.21 (16)
S1—Ag1—O1ⁱ	103.30 (3)	C1—C2—C4	116.29 (16)
S1ⁱ—Ag1—O1ⁱ	97.62 (3)	C1—C3—S1	105.36 (12)
O1—Ag1—O1ⁱ	80.24 (7)	C1—C3—H3A	110.7
C3—S1—C4	96.12 (9)	S1—C3—H3A	110.7
C3—S1—Ag1	106.45 (6)	C1—C3—H3B	110.7
C4—S1—Ag1	107.66 (6)	S1—C3—H3B	110.7
N2—O1—Ag1	110.82 (11)	H3A—C3—H3B	108.8
C1—N1—C2ⁱⁱ	114.66 (16)	C2—C4—S1	105.17 (12)
O2—N2—O1	119.74 (11)	C2—C4—H4A	110.7
O2—N2—O1ⁱⁱⁱ	119.74 (11)	S1—C4—H4A	110.7
O1—N2—O1ⁱⁱⁱ	120.5 (2)	C2—C4—H4B	110.7
N1—C1—C2	122.85 (17)	S1—C4—H4B	110.7
N1—C1—C3	120.77 (16)	H4A—C4—H4B	108.8
Ag1—O1—N2—O2	136.46 (5)	N1—C1—C3—S1	175.73 (14)
Ag1—O1—N2—O1ⁱⁱⁱ	−43.54 (5)	C2—C1—C3—S1	−5.08 (19)
C2ⁱⁱ—N1—C1—C2	0.3 (3)	C4—S1—C3—C1	7.26 (14)
C2ⁱⁱ—N1—C1—C3	179.41 (16)	Ag1—S1—C3—C1	117.73 (11)
N1—C1—C2—N1ⁱⁱ	−0.3 (3)	N1ⁱⁱ—C2—C4—S1	−175.17 (14)

C3—C1—C2—N1ⁱⁱ	−179.47 (16)	C1—C2—C4—S1	5.9 (2)
N1—C1—C2—C4	178.56 (17)	C3—S1—C4—C2	−7.54 (14)
C3—C1—C2—C4	−0.6 (2)	Ag1—S1—C4—C2	−116.99 (11)

Symmetry codes: (i) −x+1/2, y, −z+3/2; (ii) −x+1, −y+1, −z+2; (iii) −x+3/2, y, −z+3/2.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3B···O1^{iv}	0.98	2.50	3.379 (2)	150
C4—H4A···O1	0.98	2.62	3.475 (2)	146

Symmetry code: (iv) x, y−1, z.

(II)

Crystal data

[C$_{12}$H$_{16}$N$_2$S$_4$]AgNO$_3$	$F(000) = 976$
$M_r = 486.39$	$D_x = 1.933$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.0777$ (6) Å	Cell parameters from 5000 reflections
$b = 12.0654$ (7) Å	$\theta = 2.1–25.9°$
$c = 19.5725$ (18) Å	$\mu = 1.72$ mm^{-1}
$\beta = 90.446$ (10)°	$T = 293$ K
$V = 1671.3$ (2) Å^3	Plate, colourless
$Z = 4$	$0.50 \times 0.23 \times 0.08$ mm

Data collection

STOE IPDS 1 diffractometer	12808 measured reflections
Radiation source: fine-focus sealed tube	3222 independent reflections
Plane graphite monochromator	2226 reflections with $I > 2\sigma(I)$
φ rotation scans	$R_{int} = 0.051$
Absorption correction: multi-scan (MULABS; Spek, 2020)	$\theta_{max} = 25.9°$, $\theta_{min} = 2.7°$
$T_{min} = 0.939$, $T_{max} = 1.000$	$h = -8 \rightarrow 8$
	$k = -14 \rightarrow 14$
	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.029$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.059$	
$S = 0.85$	H-atom parameters constrained
3222 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2]$
208 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.61$ e Å^{-3}
	$\Delta\rho_{min} = -0.42$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ag1	0.13078 (4)	−0.29440 (2)	0.19436 (2)	0.04241 (10)
S1	0.24146 (12)	−0.10620 (8)	0.24454 (5)	0.0373 (2)
S2	0.77716 (12)	0.01162 (8)	0.28097 (4)	0.0348 (2)
S3	−0.06576 (11)	0.27177 (7)	0.42666 (4)	0.0339 (2)
S4	0.47060 (13)	0.37232 (8)	0.47535 (5)	0.0393 (2)
N1	0.1835 (4)	0.0237 (2)	0.40414 (13)	0.0291 (6)
N2	0.5521 (4)	0.0911 (2)	0.42978 (13)	0.0286 (6)
C1	0.3289 (4)	−0.0297 (3)	0.37562 (15)	0.0274 (7)
C2	0.5158 (4)	0.0053 (3)	0.38798 (15)	0.0258 (7)
C3	0.4069 (4)	0.1436 (3)	0.45887 (15)	0.0251 (7)
C4	0.2197 (4)	0.1106 (3)	0.44487 (15)	0.0263 (7)
C5	0.2793 (5)	−0.1318 (3)	0.33509 (17)	0.0358 (8)
H5A	0.165563	−0.164238	0.353851	0.043*
H5B	0.380341	−0.185522	0.340408	0.043*
C6	0.6852 (5)	−0.0512 (3)	0.35795 (16)	0.0329 (8)
H6A	0.651804	−0.127495	0.347866	0.039*
H6B	0.785052	−0.052515	0.392170	0.039*
C7	0.5692 (5)	0.0204 (3)	0.22688 (18)	0.0426 (9)
H7A	0.477204	0.067732	0.248948	0.051*
H7B	0.603872	0.055461	0.184170	0.051*
C8	0.4763 (5)	−0.0915 (3)	0.21101 (18)	0.0445 (10)
H8A	0.555159	−0.150061	0.229659	0.053*
H8B	0.471027	−0.101211	0.161836	0.053*
C9	0.0521 (4)	0.1650 (3)	0.47689 (16)	0.0307 (8)
H9A	0.092472	0.197692	0.519870	0.037*
H9B	−0.039749	0.107962	0.487395	0.037*
C10	0.1189 (5)	0.3706 (3)	0.40868 (19)	0.0465 (10)
H10A	0.208798	0.336051	0.378179	0.056*
H10B	0.063285	0.432988	0.384615	0.056*
C11	0.2260 (5)	0.4144 (3)	0.4709 (2)	0.0446 (10)
H11A	0.162698	0.389116	0.511779	0.054*
H11B	0.220446	0.494733	0.470435	0.054*
C12	0.4591 (5)	0.2326 (3)	0.50841 (16)	0.0310 (8)
H12A	0.581414	0.214425	0.528093	0.037*
H12B	0.368141	0.231524	0.545226	0.037*
O11	−0.1700 (4)	−0.2945 (3)	0.25969 (17)	0.0690 (9)
O12	−0.2807 (5)	−0.3358 (3)	0.35741 (16)	0.0861 (11)
O13	0.0187 (5)	−0.3523 (3)	0.33897 (16)	0.0757 (9)
N10	−0.1430 (5)	−0.3274 (3)	0.31906 (19)	0.0530 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.04418 (16)	0.03874 (17)	0.04419 (16)	0.00539 (15)	−0.00744 (11)	−0.00304 (14)
S1	0.0316 (5)	0.0397 (6)	0.0405 (5)	−0.0017 (4)	−0.0032 (4)	−0.0104 (4)

S2	0.0278 (5)	0.0356 (6)	0.0413 (5)	−0.0012 (4)	0.0058 (4)	−0.0033 (4)
S3	0.0279 (4)	0.0339 (5)	0.0399 (5)	0.0004 (4)	−0.0040 (3)	−0.0003 (4)
S4	0.0372 (5)	0.0287 (5)	0.0519 (6)	−0.0055 (4)	−0.0073 (4)	−0.0004 (4)
N1	0.0302 (15)	0.0290 (17)	0.0282 (14)	−0.0054 (13)	0.0028 (12)	−0.0022 (12)
N2	0.0258 (14)	0.0285 (17)	0.0316 (15)	0.0003 (12)	−0.0009 (11)	0.0027 (12)
C1	0.0330 (18)	0.0262 (19)	0.0231 (16)	−0.0051 (15)	0.0021 (14)	−0.0008 (14)
C2	0.0311 (17)	0.0220 (18)	0.0242 (16)	−0.0009 (15)	−0.0008 (13)	0.0013 (13)
C3	0.0309 (18)	0.0196 (18)	0.0249 (16)	−0.0026 (14)	−0.0009 (13)	0.0024 (13)
C4	0.0340 (18)	0.0227 (18)	0.0222 (16)	−0.0017 (15)	0.0016 (13)	0.0020 (13)
C5	0.040 (2)	0.028 (2)	0.040 (2)	−0.0070 (17)	0.0053 (16)	−0.0069 (15)
C6	0.0317 (18)	0.030 (2)	0.0373 (19)	0.0046 (15)	−0.0020 (15)	0.0016 (15)
C7	0.042 (2)	0.051 (3)	0.034 (2)	−0.0075 (19)	−0.0032 (16)	0.0043 (17)
C8	0.043 (2)	0.055 (3)	0.036 (2)	−0.0053 (19)	−0.0005 (16)	−0.0116 (17)
C9	0.0309 (17)	0.031 (2)	0.0305 (18)	−0.0019 (15)	0.0047 (14)	0.0017 (14)
C10	0.046 (2)	0.040 (2)	0.053 (2)	−0.0089 (19)	−0.0150 (18)	0.0132 (19)
C11	0.042 (2)	0.027 (2)	0.065 (3)	−0.0001 (17)	−0.0138 (19)	−0.0052 (18)
C12	0.0354 (18)	0.029 (2)	0.0286 (17)	−0.0012 (15)	−0.0050 (14)	−0.0029 (14)
O11	0.0629 (19)	0.068 (2)	0.077 (2)	0.0157 (18)	0.0216 (16)	0.0230 (19)
O12	0.085 (2)	0.104 (3)	0.070 (2)	−0.020 (2)	0.0425 (19)	−0.0283 (19)
O13	0.063 (2)	0.085 (3)	0.079 (2)	−0.0113 (19)	−0.0004 (17)	−0.0053 (18)
N10	0.055 (2)	0.039 (2)	0.066 (3)	−0.0064 (17)	0.021 (2)	−0.0154 (17)

Geometric parameters (Å, º)

Ag1—S1	2.5927 (10)	C5—H5A	0.9700
Ag1—S2[i]	2.4760 (10)	C5—H5B	0.9700
Ag1—S3[ii]	2.5382 (9)	C6—H6A	0.9700
Ag1—O11	2.492 (3)	C6—H6B	0.9700
S1—C8	1.801 (4)	C7—C8	1.533 (5)
S1—C5	1.817 (3)	C7—H7A	0.9700
S2—C7	1.809 (4)	C7—H7B	0.9700
S2—C6	1.812 (3)	C8—H8A	0.9700
S3—C10	1.805 (4)	C8—H8B	0.9700
S3—C9	1.819 (3)	C9—H9A	0.9700
S4—C11	1.806 (4)	C9—H9B	0.9700
S4—C12	1.807 (3)	C10—C11	1.524 (5)
N1—C1	1.340 (4)	C10—H10A	0.9700
N1—C4	1.341 (4)	C10—H10B	0.9700
N2—C3	1.338 (4)	C11—H11A	0.9700
N2—C2	1.343 (4)	C11—H11B	0.9700
C1—C2	1.408 (4)	C12—H12A	0.9700
C1—C5	1.505 (4)	C12—H12B	0.9700
C2—C6	1.503 (4)	O11—N10	1.241 (4)
C3—C4	1.409 (4)	O12—N10	1.239 (4)
C3—C12	1.491 (4)	O13—N10	1.243 (4)
C4—C9	1.498 (4)		
S2[i]—Ag1—S1	132.51 (3)	H6A—C6—H6B	107.5

S3ii—Ag1—S1	97.47 (3)	C8—C7—S2	114.4 (3)
S2i—Ag1—S3ii	121.65 (3)	C8—C7—H7A	108.7
O11—Ag1—S1	93.62 (8)	S2—C7—H7A	108.7
S2i—Ag1—O11	97.12 (8)	C8—C7—H7B	108.7
O11—Ag1—S3ii	109.25 (8)	S2—C7—H7B	108.7
C8—S1—C5	104.04 (16)	H7A—C7—H7B	107.6
C8—S1—Ag1	103.02 (12)	C7—C8—S1	114.1 (3)
C5—S1—Ag1	105.21 (11)	C7—C8—H8A	108.7
C7—S2—C6	102.43 (16)	S1—C8—H8A	108.7
C7—S2—Ag1iii	105.67 (13)	C7—C8—H8B	108.7
C6—S2—Ag1iii	109.21 (12)	S1—C8—H8B	108.7
C10—S3—C9	104.08 (16)	H8A—C8—H8B	107.6
C10—S3—Ag1iv	98.75 (13)	C4—C9—S3	116.5 (2)
C9—S3—Ag1iv	111.15 (11)	C4—C9—H9A	108.2
C11—S4—C12	103.52 (17)	S3—C9—H9A	108.2
C1—N1—C4	118.7 (3)	C4—C9—H9B	108.2
C3—N2—C2	118.7 (3)	S3—C9—H9B	108.2
N1—C1—C2	120.5 (3)	H9A—C9—H9B	107.3
N1—C1—C5	115.9 (3)	C11—C10—S3	115.5 (3)
C2—C1—C5	123.5 (3)	C11—C10—H10A	108.4
N2—C2—C1	120.7 (3)	S3—C10—H10A	108.4
N2—C2—C6	116.0 (3)	C11—C10—H10B	108.4
C1—C2—C6	123.2 (3)	S3—C10—H10B	108.4
N2—C3—C4	120.5 (3)	H10A—C10—H10B	107.5
N2—C3—C12	115.5 (3)	C10—C11—S4	114.3 (3)
C4—C3—C12	123.9 (3)	C10—C11—H11A	108.7
N1—C4—C3	120.8 (3)	S4—C11—H11A	108.7
N1—C4—C9	116.3 (3)	C10—C11—H11B	108.7
C3—C4—C9	122.8 (3)	S4—C11—H11B	108.7
C1—C5—S1	114.0 (2)	H11A—C11—H11B	107.6
C1—C5—H5A	108.7	C3—C12—S4	116.8 (2)
S1—C5—H5A	108.7	C3—C12—H12A	108.1
C1—C5—H5B	108.7	S4—C12—H12A	108.1
S1—C5—H5B	108.7	C3—C12—H12B	108.1
H5A—C5—H5B	107.6	S4—C12—H12B	108.1
C2—C6—S2	115.3 (2)	H12A—C12—H12B	107.3
C2—C6—H6A	108.4	N10—O11—Ag1	110.8 (2)
S2—C6—H6A	108.4	O12—N10—O11	118.5 (4)
C2—C6—H6B	108.4	O12—N10—O13	121.1 (4)
S2—C6—H6B	108.4	O11—N10—O13	120.4 (3)
C4—N1—C1—C2	−0.4 (4)	C1—C2—C6—S2	97.0 (3)
C4—N1—C1—C5	175.3 (3)	C7—S2—C6—C2	−52.5 (3)
C3—N2—C2—C1	−0.8 (4)	Ag1iii—S2—C6—C2	59.2 (3)
C3—N2—C2—C6	−179.0 (3)	C6—S2—C7—C8	−60.0 (3)
N1—C1—C2—N2	1.6 (5)	Ag1iii—S2—C7—C8	−174.3 (2)
C5—C1—C2—N2	−173.7 (3)	S2—C7—C8—S1	115.8 (3)
N1—C1—C2—C6	179.7 (3)	C5—S1—C8—C7	−76.5 (3)

C5—C1—C2—C6	4.3 (5)	Ag1—S1—C8—C7	173.9 (2)
C2—N2—C3—C4	−1.1 (4)	N1—C4—C9—S3	−86.5 (3)
C2—N2—C3—C12	175.8 (3)	C3—C4—C9—S3	96.9 (3)
C1—N1—C4—C3	−1.6 (4)	C10—S3—C9—C4	−56.6 (3)
C1—N1—C4—C9	−178.3 (3)	Ag1^{iv}—S3—C9—C4	48.7 (3)
N2—C3—C4—N1	2.4 (4)	C9—S3—C10—C11	−54.1 (3)
C12—C3—C4—N1	−174.3 (3)	Ag1^{iv}—S3—C10—C11	−168.6 (3)
N2—C3—C4—C9	178.9 (3)	S3—C10—C11—S4	113.1 (3)
C12—C3—C4—C9	2.2 (5)	C12—S4—C11—C10	−79.7 (3)
N1—C1—C5—S1	92.7 (3)	N2—C3—C12—S4	94.2 (3)
C2—C1—C5—S1	−91.7 (3)	C4—C3—C12—S4	−89.0 (3)
C8—S1—C5—C1	77.0 (3)	C11—S4—C12—C3	78.9 (3)
Ag1—S1—C5—C1	−175.0 (2)	Ag1—O11—N10—O12	−177.6 (3)
N2—C2—C6—S2	−84.9 (3)	Ag1—O11—N10—O13	1.7 (4)

Symmetry codes: (i) −x+1, y−1/2, −z+1/2; (ii) −x, y−1/2, −z+1/2; (iii) −x+1, y+1/2, −z+1/2; (iv) −x, y+1/2, −z+1/2.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5A···O13	0.97	2.51	3.239 (5)	132
C6—H6A···O12^{v}	0.97	2.56	3.442 (5)	150
C8—H8B···S4^{i}	0.97	2.74	3.696 (4)	169
C11—H11B···S4^{vi}	0.97	2.91	3.508 (4)	121
C12—H12B···O12^{vii}	0.97	2.37	3.177 (4)	140

Symmetry codes: (i) −x+1, y−1/2, −z+1/2; (v) x+1, y, z; (vi) −x+1, −y+1, −z+1; (vii) −x, −y, −z+1.