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Coordination chemistry of nitrile-functionalized mixed thia-aza macrocycles [9]aneN_2S and [9]aneNS_2 towards silver(I)

Alexander J. Blake,[a]* **Vito Lippolis**[b] **and Martin Schröder**[a,c]

[a]School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK, [b]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, S.S. 554 Bivio per Sestu, Monserrato (CA), 09042, Italy, and [c]Department of Chemistry, The University of Manchester, Manchester, M13 9PL, UK. *Correspondence e-mail: alexanderjohnblake@outlook.com

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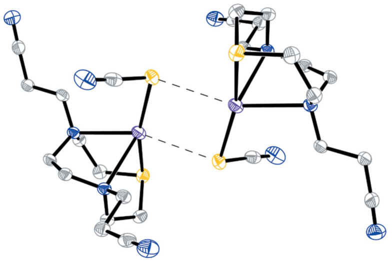
The coordination chemistry towards silver(I) of the small-ring macrocycles [9]aneN_2S (1-thia-4,7-diazacyclononane) and [9]aneNS_2 (1,4-dithia-7-azacyclononane) incorporating nitrile-functionalized pendant arms is considered both in the presence and the absence of exogenous bridging ligands. The aim is to understand the influence of the number and length of the pendant arms on the nuclearity and dimensionality of the resulting complexes. The X-ray crystal structures of the complexes bis[4,7-bis(cyanomethyl)-1-thia-4,7-diazacyclononane-κ^3N,N',S]silver(I) tetrafluoridoborate, $[Ag(C_{10}H_{16}N_4S)_2]BF_4$ or $[Ag(\mathbf{L^1})_2]BF_4$, [4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane-κ^3N,N',S](thiocyanato-κS)silver(I), $[Ag(C_{12}H_{20}N_4S)(NCS)]$ or $[Ag(\mathbf{L^2})(SCN)]$, and μ-thiocyanato-κ^2S:S-bis{[7-(2-cyanoethyl)-1,4-dithia-7-azacyclononane-κ^3N,S,S']silver(I)} tetrafluoridoborate, $[Ag_2(C_9H_{16}N_2S_2)_2(SCN)]BF_4$ or $[Ag_2(\mathbf{L^3})_2(\mu\text{-}SCN)]BF_4$, are discussed in relation to analogous compounds in the literature.



1. Introduction

In previously published articles (Tei *et al.*, 1998, 2002), we have considered the nitrile-functionalized pendant-arm derivatives of mixed-donor macrocycles as multidentate ligands for the synthesis of multidimensional polymeric complexes with silver(I). We argued that nitrile-containing pendant arms would promote exocyclic rather than endocyclic complexation, thereby preventing the formation of mononuclear complexes in favour of coordination polymers. The results confirmed this hypothesis, with the nitrile groups playing an active role in linking different silver(I) centres in the obtained polynuclear complexes whose dimensionality is strictly dependent upon the number of nitrile-functionalized pendant arms present in the ligand, upon their length, and upon the donor set and ring size of the macrocyclic framework. However, in the presence CN^-, the coordination site left free on the metal centre by the macrocyclic moiety of the nitrile-functionalized ligands in Scheme 1 [$\mathbf{L^1}$ = 4,7-bis(cyanomethyl)-1-thia-4,7-diazacyclononane, $\mathbf{L^2}$ = 4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane and $\mathbf{L^3}$ = 7-(2-cyanoethyl)-1,4-dithia-7-azacyclononane] was occupied by the exogenous anionic ligand instead of nitrile groups, thus preventing the formation of inorganic polymers involving the pendant nitriles and favouring the isolation of unusual compounds (Lippolis *et al.*, 1999; Blake *et al.*, 1998).

In particular, while the discrete binuclear complex $[Ag_2(\mathbf{L^1})_2(\mu\text{-}CN)]BF_4\cdot MeCN$, featuring a side-on two-electron (σ) μ_2-κC:κC bridging cyanide, was isolated from the reaction of $\mathbf{L^1}$, $AgBF_4$ and $^nBu_4NCN$ in a 1:1:0.5 molar ratio, the com-

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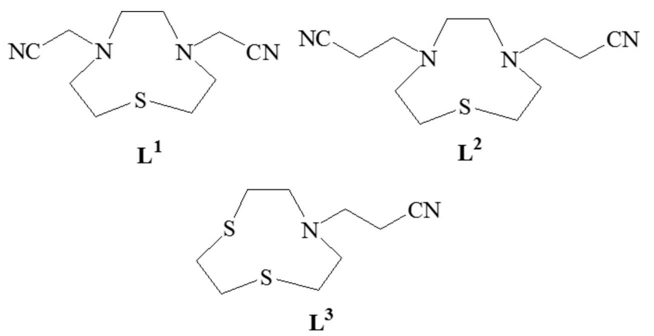
plexes $[Ag_2(\mathbf{L}^2)_2(\mu\text{-CN})]BF_4$ and $[Ag_2(\mathbf{L}^3)_2(\mu\text{-CN})]BF_4$, exhibiting a CN^- ligand bridging two metal centres in a linear four-electron ($\sigma + \pi$) μ_2-κC:κN manner (Vahrenkamp *et al.*, 1997), were isolated starting from $\mathbf{L}^2$ and $\mathbf{L}^3$, respectively, under the same experimental conditions (Lippolis *et al.*, 1999). $[Ag_2(\mathbf{L}^1)_2(\mu\text{-CN})]BF_4 \cdot MeCN$ was the first discrete binuclear complex, and is still the only one reported in the literature, featuring a pure two-electron (σ) μ_2-κC:κC bridging cyanide, to be structurally characterized. This result was initially attributed to the different length of the pendant arms in the macrocyclic ligands employed; the presence of shorter and less sterically demanding arms in $\mathbf{L}^1$ as compared to $\mathbf{L}^2$ would allow a closer approach of two $[Ag(\mathbf{L}^1)]^+$ units in the binuclear complex featuring a side-on bridging cyanide. Herein we report a further development of this chemistry from a crystallographic point of view, with the aim of better understanding the role played by the length of the aliphatic chain in nitrile-functionalized derivatives of the small-ring macrocycles [9]aneN_2S (1-thia-4,7-diazacyclononane) and [9]aneNS_2 (1,4-dithia-7-azacyclononane) in determining the coordination chemistry towards silver(I) both in the absence or in the presence of exogenous bridging ligands.



$\mathbf{L}^1$ $\mathbf{L}^2$ $\mathbf{L}^3$

Scheme 1

The compounds studied are $[Ag(\mathbf{L}^1)_2]BF_4$, $[Ag(\mathbf{L}^2)(SCN)]$ and $[Ag_2(\mathbf{L}^3)_2(\mu\text{-SCN})]BF_4$ (Scheme 2).

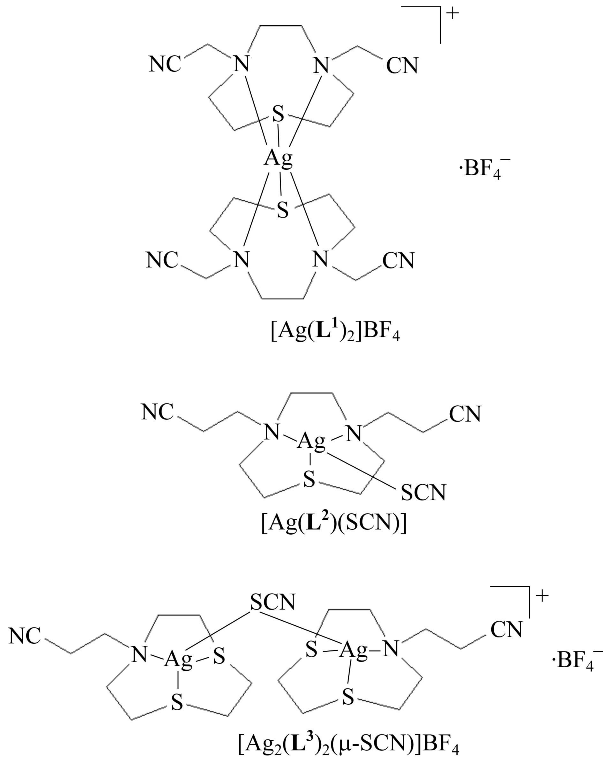
2. Experimental

2.1. Material and methods

All starting materials were obtained from Aldrich and were used without further purification. Microanalyses were performed by the University of Nottingham School of Chemistry Microanalytical Service. IR spectra were recorded as KBr discs using a PerkinElmer 598 spectrometer over the range 200–4000 cm^{-1}. Fast atom bombardment (FAB) mass spectra were recorded at the EPSRC Centre for Mass Spectroscopy at the University of Swansea, UK.

2.2. Synthesis and crystallization

4,7-Bis(cyanomethyl)-1-thia-4,7-diazacyclononane ($\mathbf{L}^1$), 4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane ($\mathbf{L}^2$) and 7-(2-cyanoethyl)-1,4-dithia-7-azacyclononane ($\mathbf{L}^3$) were prepared according to adaptations of procedures reported in the literature (Fortier & McAuley, 1989; Chak *et al.*, 1994). The experimental conditions considered for the reaction of $\mathbf{L}^2$ and $\mathbf{L}^3$ with silver(I) in the presence of thiocyanate, namely, an $\mathbf{L}/Ag^+/SCN^-$ molar ratio of 1:1:0.5, were the same as those used for the reactions in the presence of cyanate. In both cases, the aim was to favour the bridging coordination mode of the anionic ligand.



$[Ag(\mathbf{L}^1)_2]BF_4$

$[Ag(\mathbf{L}^2)(SCN)]$

$[Ag_2(\mathbf{L}^3)_2(\mu\text{-SCN})]BF_4$

Scheme 2

2.2.1. Synthesis of $[Ag(\mathbf{L}^1)_2]BF_4$. A mixture of 4,7-bis(cyanomethyl)-1-thia-4,7-diazacyclononane ($\mathbf{L}^1$) (20 mg, 0.089 mmol) and $AgBF_4$ (17.33 mg, 0.089 mmol) in MeCN (5 ml) was stirred in the dark at room temperature for 12 h. The solvent was partially removed under reduced pressure and Et_2O vapour was allowed to diffuse into the remaining solution. Colourless block-shaped crystals of the desired complex were obtained (yield 15.2 mg, 53%; m.p. 160 °C, with decomposition). Analysis calculated (%) for $[Ag(\mathbf{L}^1)_2]BF_4$, $C_{20}H_{32}AgBF_4N_8S_2$: C 37.34, H 5.01, N 17.42; found: C 37.28, H 4.99, N 17.20. FAB mass spectrum (3-NOBA) m/z: 555 and 331 for $[^{107}Ag(\mathbf{L}^1)_2]^+$ and $[^{107}Ag(\mathbf{L}^1)]^+$, respectively. IR spectrum (KBr disc) ν (cm^{-1}): 2928 (*m*), 2833 (*m*), 2243 (*s*) (ν_{CN} stretch in $\mathbf{L}^1$), 1452 (*s*), 1335 (*s*), 1223 (*w*), 1109 (*m*), 998 (*s*), 920 (*w*), 878 (*m*).

2.2.2. Synthesis of $[Ag(\mathbf{L}^2)(SCN)]$. A mixture of 4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane ($\mathbf{L}^2$) (21.7 mg, 0.086 mmol) and $AgBF_4$ (16.74 mg, 0.086 mmol) in MeCN (3 ml) was stirred in the dark at room temperature for 30 min. A solution of $^nBu_4NSCN$ (12.92 mg, 0.043 mmol) in MeCN (2.5 ml) was then added and the resulting mixture was stirred for a further 30 min in the dark at room temperature. After partial removal of the solvent under reduced pressure and filtration through a pad of celite, colourless crystals were formed upon diffusion of Et_2O vapour into the remaining solution (yield 10.5 mg; 58%; m.p. 135 °C, with decomposi-

Table 1
Experimental details.

Experiments were carried out at 150 K with Mo $K\alpha$ radiation. H-atom parameters were constrained.

	$[Ag(\mathbf{L}^1)_2]BF_4$	$[Ag(\mathbf{L}^2)(SCN)]$	$[Ag_2(\mathbf{L}^3)_2(\mu\text{-}SCN)]BF_4$
Crystal data			
Chemical formula	$[Ag(C_{10}H_{16}N_4S)_2]BF_4$	$[Ag(C_{12}H_{20}N_4S)(NCS)]$	$[Ag_2(C_9H_{16}N_2S_2)_2(SCN)]BF_4$
M_r	643.33	418.33	793.34
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$	Monoclinic, $C2/c$
a, b, c (Å)	10.1813 (6), 10.2237 (6), 15.0154 (9)	8.4426 (6), 8.5739 (6), 11.8497 (8)	28.537 (3), 8.4362 (11), 27.216 (3)
α, β, γ (°)	73.446 (2), 82.398 (2), 61.781 (2)	96.585 (1), 99.023 (1), 95.313 (1)	90, 119.940 (9), 90
V (Å^3)	1320.11 (14)	836.19 (1)	5677.6 (12)
Z	2	2	8
μ (mm^{-1})	0.98	1.46	1.79
Crystal size (mm)	0.3 × 0.2 × 0.14	0.36 × 0.30 × 0.07	0.27 × 0.15 × 0.12
Data collection			
Diffractometer	Bruker SMART CCD area-detector	Bruker SMART1000 CCD area-detector	Stoe STADI4 4-circle
Absorption correction	Multi-scan (*SADABS*; Bruker, 1996)	Integration (*SHELXTL*; Sheldrick, 2008)	Integration (*SHELXTL*; Sheldrick, 2008)
$T_{\min}$, $T_{\max}$	0.729, 0.828	0.606, 0.819	0.713, 0.822
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	13703, 6151, 5420	5159, 3668, 3401	5547, 4972, 4138
$R_{\rm int}$	0.035	0.022	0.025
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.679	0.675	0.594
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.062, 1.07	0.021, 0.055, 1.06	0.036, 0.075, 1.15
No. of reflections	6151	3668	4972
No. of parameters	328	190	326
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.46, −0.34	0.34, −0.41	0.56, −0.52

Computer programs: *SMART* (Bruker, 1998), *STADI-4* (Stoe & Cie, 1996), *SAINT* (Bruker, 1999), *X-RED* (Stoe & Cie, 1996), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2020).

tion). Analysis calculated (%) for $[Ag(\mathbf{L}^2)(SCN)]$, $C_{13}H_{20}AgN_5S_2$: C 37.32, H 4.82, N 16.74; found: C 37.30, H 4.87, N 16.65. FAB mass spectrum (3-NOBA) m/z: 359 for $[^{107}Ag(\mathbf{L}^2)]^+$. IR spectrum (KBr disc) ν (cm^{-1}): 2923 (*m*), 2824 (*m*), 2239 (*m*) (ν_{CN} stretch in $\mathbf{L}^2$), 2085 (*m*) (ν_{CN} stretch in SCN), 1472 (*m*), 1445 (*m*), 1415 (*m*), 1363 (*m*), 1306 (*w*), 1047 (*s*), 968 (*m*), 848 (*w*), 750 (*w*).

2.2.3. Synthesis of $[Ag_2(\mathbf{L}^3)_2(\mu\text{-}SCN)]BF_4$. A mixture of 7-(2-cyanoethyl)-1,4-dithia-7-azacyclononane ($\mathbf{L}^3$) (21.7 mg, 0.100 mmol) and $AgBF_4$ (19.47 mg, 0.100 mmol) in MeCN (2.5 ml) was stirred in the dark at room temperature for 30 min. A solution of ^{n}Bu$_4$NSCN (15.027 mg, 0.050 mmol) in MeCN (2.5 ml) was then added and the resulting mixture was stirred for a further 30 min in the dark at room temperature. After partial removal of the solvent under reduced pressure and filtration through a pad of celite, colourless crystals were formed upon diffusion of Et_2O vapour into the remaining solution (yield 18.3 mg; 46%; m.p. 140–142 °C). Analysis calculated (%) for $[Ag_2(\mathbf{L}^3)_2(\mu\text{-}SCN)]BF_4$, $C_{19}H_{32}Ag_2BF_4N_5S_5$: C 28.76, H 4.07, N 8.83; found: C 28.65, H 3.98, N 8.78. FAB mass spectrum (3-NOBA) m/z: 323 for $[^{107}Ag(\mathbf{L}^3)]^+$. IR spectrum (KBr disc) ν (cm^{-1}): 2911 (*m*), 2826 (*m*), 2246 (*m*) (ν_{CN} stretch in $\mathbf{L}^3$), 2105 (*m*) (ν_{CN} stretch in SCN), 1462 (*m*), 1410 (*m*), 1361 (*m*), 1303 (*m*), 1037 (*s*), 958 (*w*), 940 (*w*), 899 (*w*), 830 (*w*), 810 (*w*), 710 (*w*).

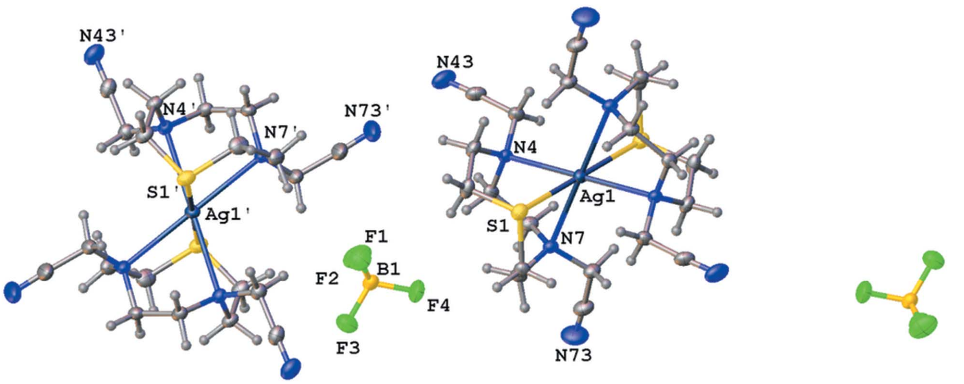


Figure 1
Two asymmetric units of complex $[Ag(\mathbf{L}^1)_2]BF_4$, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The heteroatoms of the asymmetric unit are labelled.

2.3. Refinement of X-ray data

Crystal data, data collection and structure refinement details are summarized in Table 1. Methylene H atoms were refined as riding on their parent C atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

3. Results and discussion

Following the synthetic strategy adopted in previous studies to favour the formation of inorganic polymers, we reacted $\mathbf{L^1}$ with $AgBF_4$ in MeCN using a 1:1 metal-to-ligand molar ratio. Colourless tabular crystals formed after partial removal of the solvent and subsequent diffusion of Et_2O vapour into the remaining solution. A single-crystal X-ray structure determination confirmed the product to be the discrete mononuclear Ag^I homoleptic complex $[Ag(\mathbf{L^1})_2]BF_4$. Two ligands bind facially to the metal centre *via* the tridentate macrocyclic moiety, thus conferring a distorted octahedral coordination geometry of four N-donor and two S-donor atoms (Fig. 1), with no involvement of the nitrile groups from the pendant arms in metal coordination. The sandwich complex cations lie on crystallographic inversion centres, with the asymmetric unit consisting of two half-cations and one BF_4^- anion (Z = 2). Each equatorial plane is defined by the N-donor atoms of two macrocyclic moieties [Ag1—N4 = 2.6173 (12), Ag1—N7 = 2.6822 (14), Ag1′—N4′ = 2.6363 (12) and Ag1′—N7′ = 2.6108 (13) Å], while the apical positions are occupied by the S-donor atoms [Ag1—S1 = 2.5273 (4) and Ag1′—S1′ = 2.5605 (4) Å] (Table 2). The Ag—N bond lengths are slightly longer than those reported for the sandwich complex $[Ag(Me_3[9]aneN_3)_2]PF_6$ [Ag—N = 2.543 (10) and 2.607 (7) Å; $Me_3[9]aneN_3$ = 1,4,7-trimethyl-1,4,7-triazacyclononane] (Stockheim *et al.*, 1991), while the Ag—S bond length is significantly shorter than those observed in the sandwich complex $[Ag([9]aneS_3)_2](CF_3SO_3)$ [2.696 (2)–2.753 (1) Å; $[9]aneS_3$ = 1,4,7-ththiacyclononane] (Blower *et al.*, 1989).

Table 2
Selected geometric parameters (Å, °).

$[Ag(\mathbf{L^1})_2]BF_4$			
Ag1—S1	2.5273 (4)	Ag1′—S1′	2.5605 (4)
Ag1—N4	2.6173 (12)	Ag1′—N4′	2.6363 (12)
Ag1—N7	2.6822 (14)	Ag1′—N7′	2.6108 (13)
S1—Ag1—N4	77.67 (3)	S1′—Ag1′—N4′	76.92 (3)
S1—Ag1—N7	76.40 (3)	S1′—Ag1′—N7′	76.70 (3)
N4—Ag1—N7	68.50 (4)	N7′—Ag1′—N4′	69.72 (4)
$[Ag(\mathbf{L^2})(SCN)]$			
Ag1—S1	2.5074 (5)	Ag1—N7	2.5561 (15)
Ag1—S	2.4390 (5)	C—N	1.152 (3)
Ag1—N4	2.5490 (14)	C—S	1.670 (2)
S1—Ag1—N4	79.60 (4)	S—Ag1—N7	111.02 (4)
S1—Ag1—N7	79.77 (4)	N4—Ag1—N7	71.15 (5)
S—Ag1—S1	160.21 (2)	N—C—S	177.7 (2)
S—Ag1—N4	119.16 (4)		
$[Ag_2(\mathbf{L^3})_2(\mu\text{-SCN})]BF_4$			
Ag1—Ag2	3.0716 (6)	Ag2—S1*A*	2.5329 (13)
Ag1—S4	2.6065 (13)	Ag2—S4*A*	2.6046 (13)
Ag1—S1	2.5966 (13)	Ag2—S	2.4441 (13)
Ag1—S	2.4943 (13)	Ag2—N7*A*	2.557 (4)
Ag1—N7	2.492 (4)		
S1—Ag1—S4	83.55 (4)	S1*A*—Ag2—S4*A*	86.88 (4)
S—Ag1—S4	129.95 (4)	S1*A*—Ag2—N7*A*	78.06 (9)
S—Ag1—S1	142.23 (4)	S4*A*—Ag2—Ag1	85.08 (3)
N7—Ag1—Ag2	120.33 (9)	S—Ag2—S1*A*	143.47 (4)
N7—Ag1—S4	80.45 (9)	S—Ag2—S4*A*	124.09 (4)
N7—Ag1—S1	79.96 (9)	S—Ag2—N7*A*	123.39 (9)
N7—Ag1—S	117.91 (9)	N7*A*—Ag2—S4*A*	77.95 (9)
Ag1—S—Ag2	76.91 (4)		

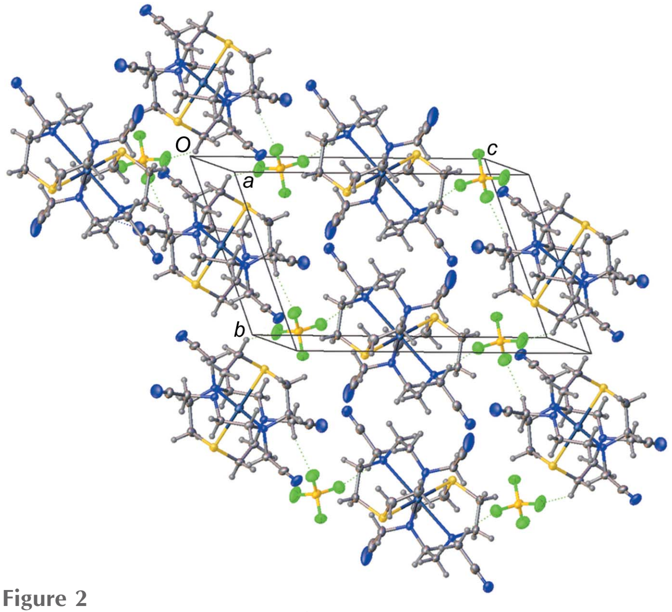


Figure 2
The extended structure of $[Ag(\mathbf{L^1})_2]BF_4$, viewed approximately along the *a* axis. The structure features C—H···F and C—H···N interactions (shown as dotted lines), which link cations and anions into layers.

The extended structure of $[Ag(\mathbf{L^1})_2]BF_4$ features C—H···N and C—H···F interactions characterized by H···*A* distances of 2.36–2.62 Å and *D*—H···*A* angles of 128–161° (see Table S1 in the supporting information). These interactions link cations and anions into chains (see Fig. 2; complementary views of the packing are available as Figs. S1 and S2 in the

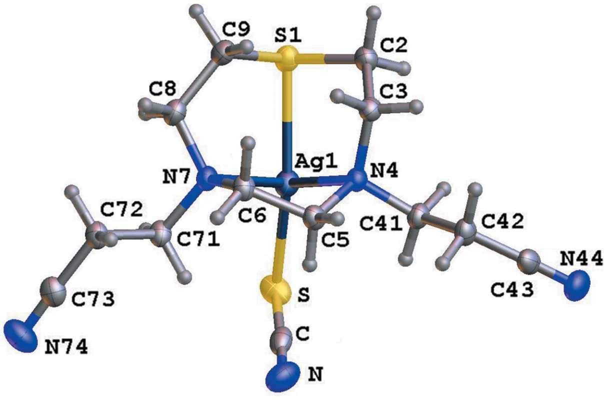


Figure 3
The asymmetric unit of complex $[Ag(\mathbf{L^2})(SCN)]BF_4$, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

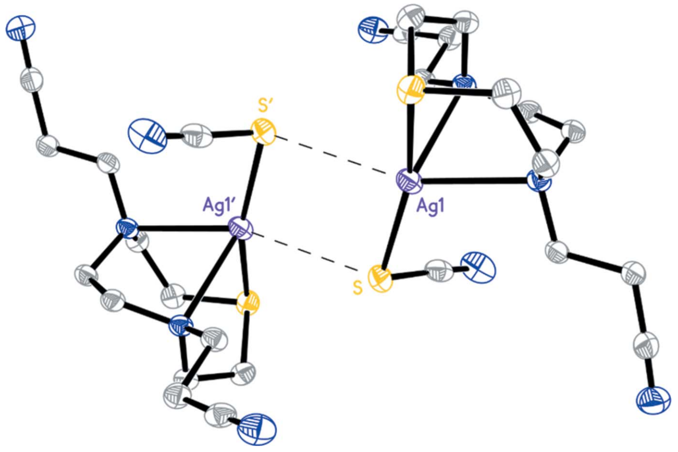


Figure 4
View of a pair of [Ag($\mathbf{L^2}$)(SCN)] molecules, showing intermolecular Ag$\cdots$S interactions. H atoms have been omitted for clarity. [Symmetry code: (′) $-x + 1, -y + 1, -z + 1$.]

supporting information) and crosslink these chains to form layers.

The formation of the mononuclear sandwich complex [Ag($\mathbf{L^1}$)$_2$]BF$_4$ upon reaction of $\mathbf{L^1}$ with silver(I) appears to support the hypothesis that longer nitrile pendant arms favour the formation of polynuclear complexes *via* bridging different metal centres that occupy different ring cavities. Thus, reaction of $\mathbf{L^2}$ with AgBF$_4$ afforded the binuclear complex [Ag$_2$($\mathbf{L^2}$)$_2$[(BF$_4$)$_2$, in which two inversion-related [Ag($\mathbf{L^2}$)]$^+$ units are held together by Ag—N bonds involving one nitrile-functionalized pendant arm from each ligand; the remaining two pendant arms are uncoordinated (Tei *et al.*, 2002). Also, the formation of a sinusoidal one-dimensional polymer is observed in {[Ag($\mathbf{L^3}$)]BF$_4$}$_\infty$, in which each Ag$^{\rm I}$ ion of the [Ag($\mathbf{L^3}$)]$^+$ repeating unit is bound by the [9]aneN$_2$S macrocyclic moiety of the ligand and by the nitrile group of a symmetry-related [Ag($\mathbf{L^3}$)]$^+$ unit (Tei *et al.*, 2002).

The observed steric influence of nitrile-functionalized pendant arms on the formation of a polynuclear silver(I) complex cannot be the same in the presence of exogenous bridging ligands. The results obtained in the presence of CN$^-$ {side-on coordination in the case of the binuclear complex cation [Ag$_2$($\mathbf{L^1}$)$_2$(μ-CN)]$^+$ and end-on coordination in the case of [Ag$_2$($\mathbf{L^2}$)$_2$(μ-CN)]$^+$ and [Ag$_2$($\mathbf{L^3}$)$_2$(μ-CN)]$^+$} seem to indicate the same trend observed in the absence of the *pseudo*-halogen (Lippolis *et al.*, 1999). In order to test this idea, we considered the reaction of $\mathbf{L^2}$ and $\mathbf{L^3}$ with NCS$^-$ that, like CN$^-$, can coordinate to metals in both terminal and bridging modes; moreover, as bridging ligands, NCS$^-$ can also link metal centres in either an end-on or a side-on bonded fashion.

Reaction of $\mathbf{L^2}$ with 1 equiv. of AgBF$_4$ in MeCN in the presence of 0.5 equiv. of ^{n}Bu$_4$NSCN was carried out under the same experimental conditions used for the reaction performed in the presence of CN$^-$. After partial removal of the solvent and filtration through a pad of celite, colourless crystals were formed upon diffusion of Et$_2$O vapour into the remaining solution. Microanalytical data suggested the formulation [Ag($\mathbf{L^2}$)(SCN)] for the product obtained and an X-ray diffraction analysis was undertaken to elucidate the coordination mode of the ligand NCS$^-$. The compound consists of mononuclear units and shows the metal centre facially coordinated to the macrocyclic moiety of $\mathbf{L^2}$ [Ag1—N4 = 2.5490 (14), Ag1—N7 = 2.5561 (15) and Ag1—S1 = 2.5074 (5) Å] and to a terminal SCN$^-$ anion ligand *via* its S-donor atom [Ag1—S 2.4390 (5) Å] in a tetrahedral geometry (Fig. 3).

The structure is very similar to that observed for [Ag([9]aneN$_2$S)Cl] (Heinzel & Mattes; 1992), in which the Ag—N and Ag—S distances [Ag—N = 2.414 (5) and Ag—S = 2.629 (2) Å] are significantly shorter and longer, respectively, than those observed in [Ag($\mathbf{L^2}$)(SCN)] and in [Ag(Me$_3$[9]aneN$_3$)(SCN)] (Stockheim *et al.*, 1991). The Ag—N distances in [Ag(Me$_3$[9]aneN$_3$)(SCN)] are comparable with those in [Ag([9]aneN$_2$S)Cl]. As observed in [Ag(Me$_3$[9]aneN$_3$)(SCN)], the structure of [Ag($\mathbf{L^2}$)(SCN)] shows molecular complex units packed pairwise, with the silver(I) ion and the S-donor from the thiocyanate ligand of two different complex units interacting in a head-to-tail manner to form a planar four-membered rhombohedral ring with intermolecular Ag$\cdots$S interactions of 3.2421 (6) Å (Fig. 4).

Presumably these interactions, rather than steric factors, are responsible for the fact that the nitrile groups are not involved in metal coordination and the thiocyanate ligand prefers to

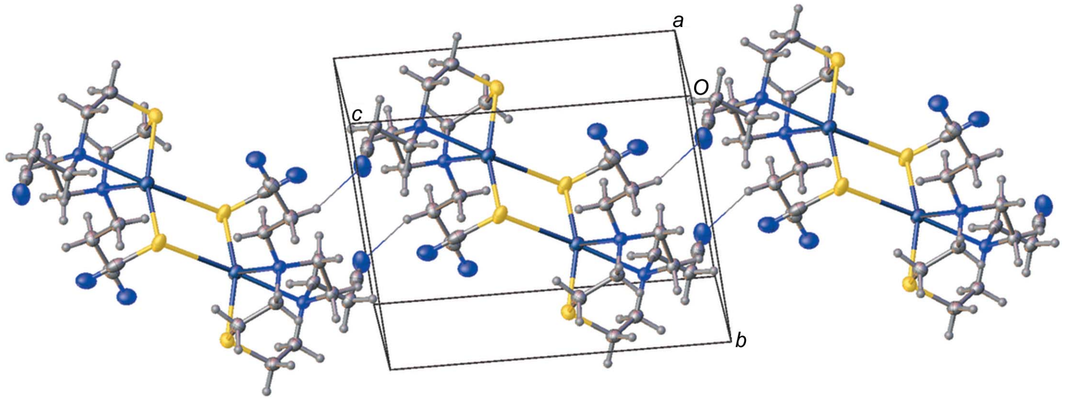


Figure 5
Partial view, approximatively along the *a* axis, of a chain of pairs of [Ag($\mathbf{L^2}$)(SCN)] molecules linked *via* C—H$\cdots$N(nitrile) interactions.

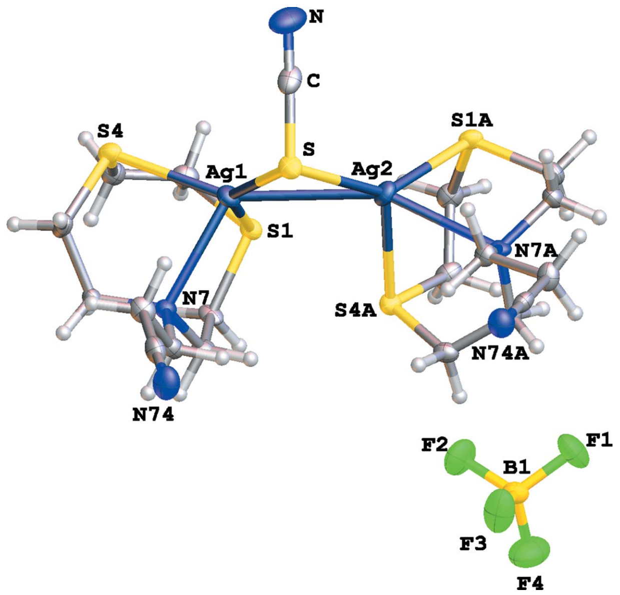


Figure 6
The asymmetric unit of complex $[Ag_2(\mathbf{L}^3)_2(\mu\text{-SCN})]BF_4$, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

coordinate the metal centre in terminal rather than in bridging mode. Furthermore, pairs of $[Ag(\mathbf{L}^2)(SCN)]$ complex units are linked into chains of molecules by C42—H42*A*···N74^i interactions [N74^i···H42*A* = 2.34 Å and C42—H42*A*···N74^i = 157°; symmetry code: (i) $-x + 1, -y + 1, -z$] (Fig. 5). These chains run parallel to the *c* axis. The C—H···N(nitrile) interactions are supported by C—H···N(thiocyanate) interactions (not shown for clarity in Fig. 5) [C72—H72*A*···N^i: N^i···H72*A* = 2.51 Å and C72—H72*A*···N^i = 142°; see Table S2 in the supporting information for short contacts in the structure].

Surprisingly, the reaction of $\mathbf{L}^3$ with $AgBF_4$ and $^n Bu_4NSCN$ under the same experimental conditions used for $[Ag(\mathbf{L}^2)(SCN)]$ afforded the binuclear complex $[Ag_2(\mathbf{L}^3)_2(\mu\text{-SCN})]BF_4$, which shows a μ_2-κS:κS bridging NCS^- ligand acting as a σ two-electron donor between two metal centres of $[Ag(\mathbf{L}^3)]^+$ complex cationic units [Ag1—S = 2.4943 (13) and Ag2—S = 2.4441 (13) Å] (Fig. 6).

The structure is very similar to that observed for the $[Ag_2(\mathbf{L}^1)_2(\mu\text{-CN})]^+$ complex cation except that $\mathbf{L}^1$ (which has two $-CH_2CN$ pendant arms) and CN^- are replaced by $\mathbf{L}^3$ (which has only one $-CH_2CH_2CN$ pendant arm) and NCS^-. The Ag1—S—Ag2 angle of 76.91 (4)° is slightly smaller than the angle at the side-on bridging cyanide [Ag1—C—Ag2 = 79.5 (3)°] in $[Ag_2(\mathbf{L}^1)_2(\mu\text{-CN})]^+$ (Lippolis *et al.*, 1999), with the Ag—Ag distance being significantly longer [3.0716 (6) Å] compared to the value of 2.7557 (10) Å in $[Ag_2(\mathbf{L}^1)_2(\mu\text{-CN})]^+$; this could be a consequence of the longer Ag—S distances compared to Ag—C [2.153 (8) and 2.155 (8) Å, respectively]. The packing in $[Ag_2(\mathbf{L}^3)_2(\mu\text{-SCN})]BF_4$ is a 3D network built up by an array of C—H···N, C—H···F and C—H···S interactions (see Fig. S3 and Table S3 in the supporting information).

The complex cation $[Ag_2(\mathbf{L}^3)_2(\mu\text{-SCN})]^+$ represents the first discrete binuclear silver(I) complex featuring a two-electron (σ) μ_2-κS:κS bridging thiocyanate. A similar coordination mode of SCN^- in discrete binuclear complexes has only been observed in the complex anion $[Hg_2(SCN)_7]^{3-}$ in $[Co(NH_3)_6][Hg_2(SCN)_7]$ (Bala *et al.*, 2006).

4. Conclusions

In this article, we have described the crystal structures of three new silver(I) complexes of nitrile-functionalized pendant-arm derivatives of the tridentate macrocyclic ligands [9]aneN$_3$, [9]aneN$_2$S and [9]aneNS$_2$, including the presence of thiocyanate (NCS^-). The results obtained, as compared to those previously reported in the presence of cyanate (CN^-), allow a better understanding of the role played by the number and length of the pendant arms in the coordination chemistry of this type of ligand towards silver(I). In general, longer more sterically-demanding nitrile-functionalized pendant arms in the macrocyclic derivatives (**L**) do not appear to prevent CN^- or NCS^- forming a side-on two-electron (σ) bridge rather than a linear four-electron ($\sigma + \pi$) one between two $[Ag(\mathbf{L})]^+$ units, provided the appropriate pseudo-halide is used, *i.e.* steric factors appear not to be responsible for the fact that CN^- shows a linear μ_2-κC:κN bridging mode in $[Ag_2(\mathbf{L}^3)_2(\mu\text{-CN})]BF_4$, whereas NCS^- forms a side-on μ_2-κS:κS bridge in the binuclear complex $[Ag_2(\mathbf{L}^3)_2(\mu\text{-SCN})]BF_4$. In fact, steric factors cannot be considered solely responsible for this because an end-on μ_2-κS:κN bridging mode for NCS^- would have allowed the two $[Ag(\mathbf{L}^3)]^+$ units to dispose themselves further apart than in the case of $[Ag_2(\mathbf{L}^3)_2(\mu\text{-CN})]^+$ where the shorter CN^- acts as a linear μ_2-κC:κN bridging donor. On the other hand, with $\mathbf{L}^2$ presenting two longer pendant arms as in $\mathbf{L}^3$, a linear μ_2-κC:κN bridging mode is observed in $[Ag_2(\mathbf{L}^2)_2(\mu\text{-CN})]BF_4$ for the cyanide ligand, while a terminal coordination mode is observed for NCS^- in the mononuclear tetrahedral complex $[Ag(\mathbf{L}^2)(SCN)]$. A side-on μ_2-κC:κN bridging mode is observed in $[Ag_2(\mathbf{L}^1)_2(\mu\text{-CN})]BF_4$, where the macrocyclic ligand $\mathbf{L}^1$ incorporates shorter pendant arms compared to $\mathbf{L}^2$ and $\mathbf{L}^3$. This result suggests that some steric effects might also come into play, in combination with electronic requirements, in the coordination chemistry of nitrile-functionalized pendant arm derivative of small tridentate macrocycles with silver(I) in the presence of anionic ligands CN^- and NCS^-.

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supporting information

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Coordination chemistry of nitrile-functionalized mixed thia-aza macrocycles [9]aneN_2S and [9]aneNS_2 towards silver(I)

Alexander J. Blake, Vito Lippolis and Martin Schröder

Computing details

Data collection: *SMART* (Bruker, 1998) for AgL12BF4, AgL2SCN; STADI-4 (Stoe & Cie, 1996) for Ag2L32mu-SCNBF4. Cell refinement: *SMART* (Bruker, 1998) for AgL12BF4, AgL2SCN; STADI-4 (Stoe & Cie, 1996) for Ag2L32mu-SCNBF4. Data reduction: *SAINT* (Bruker, 1999) for AgL12BF4, AgL2SCN; *X-RED* (Stoe & Cie, 1996) for Ag2L32mu-SCNBF4. For all structures, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

Bis[4,7-bis(cyanomethyl)-1-thia-4,7-diazacyclononane-κ^3N,N',S]silver(I) tetrafluoridoborate (AgL12BF4)

Crystal data

$[Ag(C_{10}H_{16}N_4S)_2]BF_4$
$M_r = 643.33$
Triclinic, $P\overline{1}$
$a = 10.1813$ (6) Å
$b = 10.2237$ (6) Å
$c = 15.0154$ (9) Å
$\alpha = 73.446$ (2)°
$\beta = 82.398$ (2)°
$\gamma = 61.781$ (2)°
$V = 1320.11$ (14) Å^3

$Z = 2$
$F(000) = 656$
$D_x = 1.618$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4462 reflections
$\theta = 2.3–28.8$°
$\mu = 0.98$ mm^{-1}
$T = 150$ K
Tablet, colourless
0.3 × 0.2 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: X-ray
Graphite monochromator
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 1996}
$T_{min} = 0.729$, $T_{max} = 0.828$

6151 measured reflections
13703 independent reflections
5420 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 28.8$°, $\theta_{min} = 2.3$°
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 12$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.062$
$S = 1.07$
6151 reflections

328 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

$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ 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.

Refinement. A small number of predominantly low-angle reflections showed poor agreement and were suppressed individually. There were no other systematic trends and the reasons for the poor agreement were not pursued. Diffraction data were collected on Stoe STADI4 4-circle and Bruker SMART CCD area detector diffractometers. Structures were solved by direct methods and developed by iterative cycles of least-squares refinement on F^2 and difference Fourier synthesis.

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

	x	y	z	U_{iso}*/U_{eq}
Ag1′	0.000000	1.000000	0.500000	0.02157 (5)
S1	0.80965 (5)	0.73691 (4)	0.89254 (3)	0.02367 (9)
C2	0.7080 (2)	0.66111 (19)	0.84889 (11)	0.0288 (4)
H2A	0.607906	0.695424	0.877628	0.035*
H2B	0.693997	0.706560	0.781044	0.035*
C3	0.78180 (19)	0.48679 (18)	0.86677 (10)	0.0252 (3)
H3A	0.713163	0.458039	0.845737	0.030*
H3B	0.873060	0.454056	0.828479	0.030*
N4	0.82224 (14)	0.40209 (14)	0.96400 (8)	0.0187 (3)
C5	0.69353 (17)	0.43080 (18)	1.02663 (11)	0.0223 (3)
H5A	0.670968	0.342854	1.040685	0.027*
H5B	0.605698	0.523292	0.994610	0.027*
C6	0.71893 (18)	0.45403 (18)	1.11751 (11)	0.0225 (3)
H6A	0.628725	0.472071	1.156554	0.027*
H6B	0.802780	0.359104	1.151443	0.027*
N7	0.75219 (14)	0.58322 (14)	1.10358 (8)	0.0195 (3)
C8	0.68686 (18)	0.82805 (18)	0.97989 (11)	0.0239 (3)
H8A	0.739632	0.865178	1.009359	0.029*
H8B	0.598490	0.919414	0.947553	0.029*
C9	0.63217 (17)	0.73218 (17)	1.05647 (11)	0.0235 (3)
H9A	0.578197	0.791050	1.103106	0.028*
H9B	0.560508	0.713840	1.029639	0.028*
C41	0.91605 (18)	0.23839 (18)	0.97407 (12)	0.0257 (3)
H41C	0.946423	0.187697	1.039954	0.031*
H41D	1.007482	0.222817	0.936645	0.031*
C42	0.8399 (2)	0.16515 (19)	0.94421 (12)	0.0287 (4)
N43	0.7762 (2)	0.11560 (19)	0.91955 (11)	0.0406 (4)
C71	0.79990 (18)	0.58746 (19)	1.18970 (10)	0.0250 (3)
H71C	0.828128	0.671450	1.176321	0.030*

H71D	0.889447	0.489696	1.213719	0.030*
C72	0.6831 (2)	0.6111 (2)	1.26223 (11)	0.0319 (4)
N73	0.5894 (2)	0.6280 (2)	1.31473 (11)	0.0499 (5)
Ag1	1.000000	0.500000	1.000000	0.02228 (5)
S1′	0.10514 (5)	1.09797 (5)	0.34563 (3)	0.02568 (9)
C2′	0.0767 (2)	0.98966 (19)	0.27946 (10)	0.0264 (3)
H2′A	−0.031759	1.033563	0.269579	0.032*
H2′B	0.122681	1.005841	0.217583	0.032*
C3′	0.13787 (18)	0.81697 (18)	0.32141 (10)	0.0230 (3)
H3′A	0.106138	0.773825	0.282131	0.028*
H3′B	0.248144	0.768802	0.320401	0.028*
N4′	0.08854 (14)	0.77649 (14)	0.41728 (8)	0.0203 (3)
C5′	0.20750 (17)	0.65164 (17)	0.48137 (10)	0.0230 (3)
H5′A	0.247413	0.556719	0.459982	0.028*
H5′B	0.164196	0.632522	0.543841	0.028*
C6′	0.33462 (18)	0.68556 (18)	0.48879 (11)	0.0238 (3)
H6′A	0.409806	0.597136	0.532877	0.029*
H6′B	0.382879	0.696731	0.427293	0.029*
N7′	0.28727 (14)	0.82627 (15)	0.52028 (9)	0.0220 (3)
C8′	0.35356 (19)	0.9247 (2)	0.46700 (12)	0.0293 (4)
H8′A	0.463408	0.863294	0.469830	0.035*
H8′B	0.326722	1.008418	0.497214	0.035*
C9′	0.3061 (2)	0.9960 (2)	0.36514 (12)	0.0316 (4)
H9′A	0.350110	0.913493	0.332084	0.038*
H9′B	0.348054	1.068318	0.337295	0.038*
C41′	−0.03903 (18)	0.74723 (19)	0.42178 (11)	0.0250 (3)
H41A	−0.120886	0.839174	0.384023	0.030*
H41B	−0.073772	0.732035	0.486932	0.030*
C42′	−0.00916 (19)	0.6118 (2)	0.38874 (11)	0.0282 (4)
N43′	0.01303 (19)	0.50939 (19)	0.36215 (11)	0.0378 (4)
C71′	0.31270 (19)	0.7887 (2)	0.61963 (11)	0.0291 (4)
H71A	0.258848	0.730041	0.653272	0.035*
H71B	0.270607	0.885113	0.639567	0.035*
C72′	0.4724 (2)	0.6977 (2)	0.64596 (13)	0.0433 (5)
N73′	0.5960 (2)	0.6277 (3)	0.66227 (15)	0.0718 (7)
B1	0.2911 (2)	0.9973 (2)	0.79979 (14)	0.0293 (4)
F1	0.28390 (16)	0.86125 (13)	0.81549 (8)	0.0536 (3)
F2	0.33708 (13)	1.03340 (13)	0.70886 (8)	0.0448 (3)
F3	0.15010 (12)	1.11335 (13)	0.81049 (9)	0.0483 (3)
F4	0.38827 (14)	0.98516 (16)	0.86048 (9)	0.0616 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1′	0.02112 (9)	0.02284 (9)	0.01874 (8)	−0.00723 (7)	0.00187 (6)	−0.00835 (6)
S1	0.0314 (2)	0.02153 (19)	0.02038 (18)	−0.01508 (17)	−0.00034 (15)	−0.00316 (14)
C2	0.0373 (10)	0.0247 (8)	0.0259 (8)	−0.0160 (8)	−0.0122 (7)	0.0000 (7)
C3	0.0323 (9)	0.0277 (8)	0.0204 (7)	−0.0163 (7)	−0.0037 (6)	−0.0068 (6)

N4	0.0208 (6)	0.0158 (6)	0.0201 (6)	−0.0081 (5)	−0.0002 (5)	−0.0058 (5)
C5	0.0212 (8)	0.0210 (8)	0.0279 (8)	−0.0120 (6)	0.0017 (6)	−0.0073 (6)
C6	0.0250 (8)	0.0218 (8)	0.0222 (7)	−0.0128 (7)	0.0055 (6)	−0.0064 (6)
N7	0.0221 (7)	0.0179 (6)	0.0196 (6)	−0.0095 (5)	0.0025 (5)	−0.0068 (5)
C8	0.0253 (8)	0.0159 (7)	0.0286 (8)	−0.0073 (6)	−0.0031 (6)	−0.0052 (6)
C9	0.0200 (8)	0.0196 (8)	0.0292 (8)	−0.0065 (6)	0.0029 (6)	−0.0094 (6)
C41	0.0246 (8)	0.0197 (8)	0.0310 (8)	−0.0068 (7)	−0.0016 (7)	−0.0091 (6)
C42	0.0360 (10)	0.0196 (8)	0.0299 (8)	−0.0118 (7)	0.0060 (7)	−0.0098 (6)
N43	0.0561 (11)	0.0391 (9)	0.0428 (9)	−0.0320 (9)	0.0111 (8)	−0.0203 (7)
C71	0.0276 (8)	0.0282 (8)	0.0218 (7)	−0.0138 (7)	0.0050 (6)	−0.0106 (6)
C72	0.0408 (10)	0.0314 (9)	0.0240 (8)	−0.0160 (8)	0.0058 (7)	−0.0114 (7)
N73	0.0547 (11)	0.0539 (11)	0.0350 (9)	−0.0227 (10)	0.0207 (8)	−0.0160 (8)
Ag1	0.01716 (9)	0.02577 (10)	0.02614 (9)	−0.00879 (7)	0.00062 (6)	−0.01193 (7)
S1′	0.0355 (2)	0.0231 (2)	0.02031 (18)	−0.01553 (18)	0.00362 (16)	−0.00607 (15)
C2′	0.0380 (9)	0.0268 (8)	0.0166 (7)	−0.0171 (8)	0.0006 (6)	−0.0046 (6)
C3′	0.0290 (8)	0.0243 (8)	0.0180 (7)	−0.0130 (7)	0.0024 (6)	−0.0084 (6)
N4′	0.0241 (7)	0.0201 (6)	0.0169 (6)	−0.0102 (5)	−0.0014 (5)	−0.0043 (5)
C5′	0.0284 (8)	0.0177 (7)	0.0203 (7)	−0.0075 (7)	−0.0026 (6)	−0.0056 (6)
C6′	0.0221 (8)	0.0234 (8)	0.0230 (7)	−0.0054 (7)	0.0003 (6)	−0.0108 (6)
N7′	0.0208 (7)	0.0239 (7)	0.0213 (6)	−0.0076 (6)	−0.0001 (5)	−0.0105 (5)
C8′	0.0259 (9)	0.0349 (10)	0.0341 (9)	−0.0169 (8)	0.0040 (7)	−0.0150 (7)
C9′	0.0327 (9)	0.0371 (10)	0.0319 (9)	−0.0227 (8)	0.0097 (7)	−0.0107 (7)
C41′	0.0280 (8)	0.0242 (8)	0.0231 (8)	−0.0123 (7)	−0.0009 (6)	−0.0055 (6)
C42′	0.0339 (9)	0.0319 (9)	0.0238 (8)	−0.0201 (8)	−0.0032 (7)	−0.0033 (7)
N43′	0.0520 (10)	0.0380 (9)	0.0341 (8)	−0.0281 (8)	−0.0014 (7)	−0.0103 (7)
C71′	0.0261 (9)	0.0319 (9)	0.0247 (8)	−0.0052 (7)	−0.0037 (6)	−0.0134 (7)
C72′	0.0351 (11)	0.0521 (12)	0.0371 (10)	−0.0053 (9)	−0.0099 (8)	−0.0253 (9)
N73′	0.0368 (11)	0.0989 (17)	0.0652 (13)	0.0017 (11)	−0.0190 (9)	−0.0509 (13)
B1	0.0315 (10)	0.0238 (9)	0.0314 (10)	−0.0075 (8)	−0.0075 (8)	−0.0113 (8)
F1	0.0917 (10)	0.0313 (6)	0.0421 (6)	−0.0330 (7)	−0.0030 (6)	−0.0055 (5)
F2	0.0504 (7)	0.0477 (7)	0.0391 (6)	−0.0267 (6)	0.0020 (5)	−0.0085 (5)
F3	0.0328 (6)	0.0443 (7)	0.0628 (8)	−0.0073 (5)	−0.0011 (5)	−0.0246 (6)
F4	0.0453 (7)	0.0756 (9)	0.0647 (8)	−0.0106 (7)	−0.0226 (6)	−0.0396 (7)

Geometric parameters (Å, º)

Ag1′—S1′	2.5605 (4)	C71—C72	1.481 (2)
Ag1′—S1′^{i}	2.5606 (4)	C72—N73	1.133 (2)
Ag1′—N4′	2.6363 (12)	S1′—C2′	1.8174 (16)
Ag1′—N4′^{i}	2.6363 (12)	S1′—C9′	1.8237 (18)
Ag1′—N7′^{i}	2.6108 (13)	C2′—H2′A	0.9900
Ag1′—N7′	2.6108 (13)	C2′—H2′B	0.9900
S1—C2	1.8242 (17)	C2′—C3′	1.527 (2)
S1—C8	1.8200 (17)	C3′—H3′A	0.9900
S1—Ag1	2.5273 (4)	C3′—H3′B	0.9900
C2—H2A	0.9900	C3′—N4′	1.4702 (18)
C2—H2B	0.9900	N4′—C5′	1.4727 (18)
C2—C3	1.526 (2)	N4′—C41′	1.454 (2)

C3—H3A	0.9900	C5′—H5′A	0.9900
C3—H3B	0.9900	C5′—H5′B	0.9900
C3—N4	1.4670 (19)	C5′—C6′	1.514 (2)
N4—C5	1.4681 (19)	C6′—H6′A	0.9900
N4—C41	1.4555 (19)	C6′—H6′B	0.9900
N4—Ag1	2.6173 (12)	C6′—N7′	1.482 (2)
C5—H5A	0.9900	N7′—C8′	1.466 (2)
C5—H5B	0.9900	N7′—C71′	1.4565 (19)
C5—C6	1.524 (2)	C8′—H8′A	0.9900
C6—H6A	0.9900	C8′—H8′B	0.9900
C6—H6B	0.9900	C8′—C9′	1.527 (2)
C6—N7	1.4661 (19)	C9′—H9′A	0.9900
N7—C9	1.4723 (19)	C9′—H9′B	0.9900
N7—C71	1.4589 (19)	C41′—H41A	0.9900
C8—H8A	0.9900	C41′—H41B	0.9900
C8—H8B	0.9900	C41′—C42′	1.486 (2)
C8—C9	1.516 (2)	C42′—N43′	1.139 (2)
C9—H9A	0.9900	C71′—H71A	0.9900
C9—H9B	0.9900	C71′—H71B	0.9900
C41—H41C	0.9900	C71′—C72′	1.482 (2)
C41—H41D	0.9900	C72′—N73′	1.134 (2)
C41—C42	1.482 (2)	B1—F1	1.379 (2)
C42—N43	1.138 (2)	B1—F2	1.388 (2)
C71—H71C	0.9900	B1—F3	1.390 (2)
C71—H71D	0.9900	B1—F4	1.372 (2)

S1′—Ag1′—S1′^{i}	180.0	S1—Ag1—S1^{ii}	180.0
S1′—Ag1′—N4′	76.92 (3)	S1—Ag1—N4	77.67 (3)
S1′^{i}—Ag1′—N4′	103.08 (3)	S1^{ii}—Ag1—N4	102.33 (3)
S1′—Ag1′—N4′^{i}	103.08 (3)	S1—Ag1—N4^{ii}	102.33 (3)
S1′^{i}—Ag1′—N4′^{i}	76.92 (3)	S1^{ii}—Ag1—N4^{ii}	77.67 (3)
S1′—Ag1′—N7′^{i}	103.30 (3)	N4^{ii}—Ag1—N4	180.0
S1′—Ag1′—N7′	76.70 (3)	C2′—S1′—Ag1′	97.19 (5)
S1′^{i}—Ag1′—N7′^{i}	76.70 (3)	C2′—S1′—C9′	102.79 (8)
S1′^{i}—Ag1′—N7′	103.30 (3)	C9′—S1′—Ag1′	103.55 (6)
N4′^{i}—Ag1′—N4′	180.0	S1′—C2′—H2′A	108.0
N7′^{i}—Ag1′—N4′	110.28 (4)	S1′—C2′—H2′B	108.0
N7′—Ag1′—N4′	69.72 (4)	H2′A—C2′—H2′B	107.3
N7′^{i}—Ag1′—N4′^{i}	69.72 (4)	C3′—C2′—S1′	117.00 (11)
N7′—Ag1′—N4′^{i}	110.28 (4)	C3′—C2′—H2′A	108.0
N7′^{i}—Ag1′—N7′	180.0	C3′—C2′—H2′B	108.0
C2—S1—Ag1	102.58 (5)	C2′—C3′—H3′A	108.8
C8—S1—C2	104.31 (8)	C2′—C3′—H3′B	108.8
C8—S1—Ag1	98.56 (5)	H3′A—C3′—H3′B	107.7
S1—C2—H2A	108.4	N4′—C3′—C2′	113.64 (13)
S1—C2—H2B	108.4	N4′—C3′—H3′A	108.8
H2A—C2—H2B	107.5	N4′—C3′—H3′B	108.8
C3—C2—S1	115.46 (11)	C3′—N4′—Ag1′	112.22 (9)

C3—C2—H2A	108.4	C3′—N4′—C5′	114.60 (12)
C3—C2—H2B	108.4	C5′—N4′—Ag1′	100.41 (8)
C2—C3—H3A	108.5	C41′—N4′—Ag1′	104.94 (9)
C2—C3—H3B	108.5	C41′—N4′—C3′	112.44 (12)
H3A—C3—H3B	107.5	C41′—N4′—C5′	111.21 (12)
N4—C3—C2	114.90 (13)	N4′—C5′—H5′A	108.9
N4—C3—H3A	108.5	N4′—C5′—H5′B	108.9
N4—C3—H3B	108.5	N4′—C5′—C6′	113.43 (13)
C3—N4—C5	113.57 (12)	H5′A—C5′—H5′B	107.7
C3—N4—Ag1	101.77 (9)	C6′—C5′—H5′A	108.9
C5—N4—Ag1	112.87 (9)	C6′—C5′—H5′B	108.9
C41—N4—C3	112.17 (12)	C5′—C6′—H6′A	108.9
C41—N4—C5	111.24 (12)	C5′—C6′—H6′B	108.9
C41—N4—Ag1	104.52 (9)	H6′A—C6′—H6′B	107.7
N4—C5—H5A	109.0	N7′—C6′—C5′	113.51 (13)
N4—C5—H5B	109.0	N7′—C6′—H6′A	108.9
N4—C5—C6	113.06 (12)	N7′—C6′—H6′B	108.9
H5A—C5—H5B	107.8	C6′—N7′—Ag1′	110.86 (9)
C6—C5—H5A	109.0	C8′—N7′—Ag1′	104.80 (9)
C6—C5—H5B	109.0	C8′—N7′—C6′	113.74 (13)
C5—C6—H6A	109.0	C71′—N7′—Ag1′	104.38 (9)
C5—C6—H6B	109.0	C71′—N7′—C6′	110.96 (13)
H6A—C6—H6B	107.8	C71′—N7′—C8′	111.53 (13)
N7—C6—C5	112.88 (12)	N7′—C8′—H8′A	108.5
N7—C6—H6A	109.0	N7′—C8′—H8′B	108.5
N7—C6—H6B	109.0	N7′—C8′—C9′	114.91 (13)
C6—N7—C9	113.82 (12)	H8′A—C8′—H8′B	107.5
C71—N7—C6	111.68 (12)	C9′—C8′—H8′A	108.5
C71—N7—C9	112.43 (12)	C9′—C8′—H8′B	108.5
S1—C8—H8A	107.9	S1′—C9′—H9′A	108.6
S1—C8—H8B	107.9	S1′—C9′—H9′B	108.6
H8A—C8—H8B	107.2	C8′—C9′—S1′	114.86 (12)
C9—C8—S1	117.58 (11)	C8′—C9′—H9′A	108.6
C9—C8—H8A	107.9	C8′—C9′—H9′B	108.6
C9—C8—H8B	107.9	H9′A—C9′—H9′B	107.5
N7—C9—C8	113.72 (13)	N4′—C41′—H41A	108.6
N7—C9—H9A	108.8	N4′—C41′—H41B	108.6
N7—C9—H9B	108.8	N4′—C41′—C42′	114.51 (14)
C8—C9—H9A	108.8	H41A—C41′—H41B	107.6
C8—C9—H9B	108.8	C42′—C41′—H41A	108.6
H9A—C9—H9B	107.7	C42′—C41′—H41B	108.6
N4—C41—H41C	109.1	N43′—C42′—C41′	179.01 (18)
N4—C41—H41D	109.1	N7′—C71′—H71A	108.9
N4—C41—C42	112.62 (13)	N7′—C71′—H71B	108.9
H41C—C41—H41D	107.8	N7′—C71′—C72′	113.33 (15)
C42—C41—H41C	109.1	H71A—C71′—H71B	107.7
C42—C41—H41D	109.1	C72′—C71′—H71A	108.9
N43—C42—C41	176.78 (19)	C72′—C71′—H71B	108.9

N7—C71—H71C	109.0	N73′—C72′—C71′	177.1 (2)
N7—C71—H71D	109.0	F1—B1—F2	108.17 (14)
N7—C71—C72	112.90 (14)	F1—B1—F3	109.32 (17)
H71C—C71—H71D	107.8	F2—B1—F3	108.64 (15)
C72—C71—H71C	109.0	F4—B1—F1	111.04 (16)
C72—C71—H71D	109.0	F4—B1—F2	110.29 (17)
N73—C72—C71	176.3 (2)	F4—B1—F3	109.33 (15)

Ag1′—S1′—C2′—C3′	−51.77 (13)	Ag1—S1—C2—C3	−13.93 (14)
Ag1′—S1′—C9′—C8′	−17.07 (14)	Ag1—S1—C8—C9	−51.59 (12)
Ag1′—N4′—C5′—C6′	−61.91 (13)	Ag1—N4—C5—C6	−21.40 (15)
Ag1′—N4′—C41′—C42′	−173.20 (10)	Ag1—N4—C41—C42	−172.44 (11)
Ag1′—N7′—C8′—C9′	−55.84 (15)	S1′—C2′—C3′—N4′	52.76 (17)
Ag1′—N7′—C71′—C72′	−176.18 (13)	C2′—S1′—C9′—C8′	−117.84 (13)
S1—C2—C3—N4	52.98 (19)	C2′—C3′—N4′—Ag1′	−21.06 (15)
S1—C8—C9—N7	51.09 (17)	C2′—C3′—N4′—C5′	−134.74 (13)
C2—S1—C8—C9	53.82 (13)	C2′—C3′—N4′—C41′	96.97 (16)
C2—C3—N4—C5	63.48 (17)	C3′—N4′—C5′—C6′	58.55 (17)
C2—C3—N4—C41	−169.32 (14)	C3′—N4′—C41′—C42′	64.55 (17)
C2—C3—N4—Ag1	−58.13 (14)	N4′—C5′—C6′—N7′	58.50 (17)
C3—N4—C5—C6	−136.60 (13)	C5′—N4′—C41′—C42′	−65.49 (16)
C3—N4—C41—C42	−62.98 (18)	C5′—C6′—N7′—Ag1′	−17.74 (15)
N4—C5—C6—N7	59.09 (17)	C5′—C6′—N7′—C8′	−135.52 (14)
C5—N4—C41—C42	65.45 (17)	C5′—C6′—N7′—C71′	97.76 (15)
C5—C6—N7—C9	60.78 (17)	C6′—N7′—C8′—C9′	65.39 (18)
C5—C6—N7—C71	−170.60 (13)	C6′—N7′—C71′—C72′	64.36 (19)
C6—N7—C9—C8	−134.70 (14)	N7′—C8′—C9′—S1′	52.39 (19)
C6—N7—C71—C72	−62.77 (17)	C8′—N7′—C71′—C72′	−63.56 (19)
C8—S1—C2—C3	−116.31 (13)	C9′—S1′—C2′—C3′	53.94 (14)
C9—N7—C71—C72	66.59 (17)	C41′—N4′—C5′—C6′	−172.54 (12)
C41—N4—C5—C6	95.72 (15)	C71′—N7′—C8′—C9′	−168.20 (14)
C71—N7—C9—C8	97.06 (15)		

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

[4,7-Bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane-\ κ^3*N*,*N*′,*S*](thiocyanato-κ*S*)silver(I) (AgL2SCN)

Crystal data

$[Ag(C_{12}H_{20}N_4S)(NCS)]$
M_r = 418.33
Triclinic, $P\bar{1}$
a = 8.4426 (6) Å
b = 8.5739 (6) Å
c = 11.8497 (8) Å
α = 96.585 (1)°
β = 99.023 (1)°
γ = 95.313 (1)°
V = 836.19 (1) Å^3

Z = 2
F(000) = 424
D_x = 1.661 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4102 reflections
θ = 2.4–28.7°
μ = 1.46 mm^{-1}
T = 150 K
Block, colourless
0.36 × 0.30 × 0.07 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
Graphite monochromator
Detector resolution: 8.336 pixels mm^{-1}
ω scans
Absorption correction: integration (SHELXTL; Sheldrick, 2008)
$T_{\min} = 0.606$, $T_{\max} = 0.819$
3668 measured reflections
5159 independent reflections
3401 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.022$
$\theta_{\max} = 28.7°$, $\theta_{\min} = 1.8°$
$h = -11 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.055$
$S = 1.06$
3668 reflections
190 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
$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 0.1835P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.41$ 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.

Refinement. Diffraction data were collected on Stoe STADI4 4-circle and Bruker SMART CCD area detector diffractometers. Structures were solved by direct methods and developed by iterative cycles of least-squares refinement on F^2 and difference Fourier synthesis.

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

	x	y	z	U_{iso}*/U_{eq}
Ag1	0.45271 (2)	0.67967 (2)	0.39303 (2)	0.02735 (6)
C	0.5932 (2)	0.4009 (2)	0.26281 (19)	0.0313 (4)
N	0.5567 (2)	0.3379 (2)	0.16981 (19)	0.0448 (5)
S1	0.30887 (6)	0.91065 (6)	0.45249 (4)	0.02851 (11)
C2	0.1077 (2)	0.8015 (2)	0.41856 (16)	0.0284 (4)
H2A	0.099204	0.725699	0.474927	0.034*
H2B	0.027710	0.877085	0.429162	0.034*
S	0.65402 (7)	0.49300 (7)	0.39676 (4)	0.03595 (12)
C3	0.0617 (2)	0.7106 (2)	0.29747 (16)	0.0248 (4)
H3A	−0.046607	0.651542	0.290188	0.030*
H3B	0.054769	0.787191	0.240856	0.030*
N4	0.17585 (17)	0.59921 (17)	0.26873 (13)	0.0223 (3)
C5	0.2127 (2)	0.5974 (2)	0.15067 (15)	0.0244 (4)
H5A	0.111349	0.567238	0.094771	0.029*
H5B	0.285671	0.515680	0.137477	0.029*
C6	0.2913 (2)	0.7554 (2)	0.12755 (15)	0.0243 (4)
H6A	0.320174	0.742555	0.049455	0.029*

H6B	0.212044	0.833452	0.128798	0.029*
N7	0.43751 (17)	0.81746 (17)	0.21205 (13)	0.0222 (3)
C8	0.4433 (2)	0.9845 (2)	0.25684 (16)	0.0262 (4)
H8A	0.429733	1.045962	0.190860	0.031*
H8B	0.551691	1.020002	0.302759	0.031*
C71	0.5874 (2)	0.7824 (2)	0.17176 (16)	0.0241 (4)
H71A	0.577751	0.668412	0.142763	0.029*
H71B	0.677022	0.803938	0.238190	0.029*
C72	0.6311 (2)	0.8775 (2)	0.07605 (16)	0.0261 (4)
H72A	0.543288	0.855754	0.008450	0.031*
H72B	0.642522	0.991918	0.104194	0.031*
C73	0.7826 (2)	0.8348 (2)	0.04165 (16)	0.0304 (4)
N74	0.8999 (2)	0.7988 (3)	0.01779 (17)	0.0445 (5)
C41	0.1307 (2)	0.4406 (2)	0.29564 (16)	0.0253 (4)
H41A	0.111982	0.448886	0.376417	0.030*
H41B	0.222344	0.377595	0.289955	0.030*
C42	−0.0216 (2)	0.3510 (2)	0.21647 (16)	0.0277 (4)
H42A	−0.111695	0.417330	0.215439	0.033*
H42B	0.000236	0.330067	0.136780	0.033*
C43	−0.0679 (2)	0.2013 (2)	0.25739 (17)	0.0283 (4)
N44	−0.1000 (2)	0.0852 (2)	0.29014 (16)	0.0380 (4)
C9	0.3168 (2)	1.0231 (2)	0.33171 (17)	0.0290 (4)
H9A	0.209310	1.005667	0.281911	0.035*
H9B	0.337299	1.136793	0.362339	0.035*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.02301 (8)	0.02802 (9)	0.03002 (9)	0.00191 (6)	−0.00023 (6)	0.00685 (6)
C	0.0219 (9)	0.0251 (9)	0.0493 (13)	0.0034 (7)	0.0053 (9)	0.0149 (9)
N	0.0426 (11)	0.0317 (9)	0.0544 (12)	0.0026 (8)	−0.0034 (9)	−0.0016 (8)
S1	0.0299 (2)	0.0280 (2)	0.0258 (2)	−0.00200 (19)	0.00382 (19)	0.00125 (17)
C2	0.0266 (9)	0.0286 (9)	0.0303 (10)	0.0004 (8)	0.0082 (8)	0.0029 (7)
S	0.0347 (3)	0.0463 (3)	0.0320 (3)	0.0160 (2)	0.0066 (2)	0.0164 (2)
C3	0.0208 (8)	0.0243 (9)	0.0292 (9)	0.0023 (7)	0.0036 (7)	0.0038 (7)
N4	0.0185 (7)	0.0223 (7)	0.0258 (7)	0.0002 (6)	0.0026 (6)	0.0044 (6)
C5	0.0195 (8)	0.0267 (9)	0.0252 (9)	−0.0003 (7)	0.0017 (7)	0.0014 (7)
C6	0.0184 (8)	0.0283 (9)	0.0254 (9)	0.0002 (7)	0.0004 (7)	0.0060 (7)
N7	0.0179 (7)	0.0230 (7)	0.0244 (7)	−0.0005 (6)	0.0007 (6)	0.0041 (6)
C8	0.0262 (9)	0.0231 (9)	0.0282 (9)	−0.0008 (7)	0.0021 (7)	0.0051 (7)
C71	0.0188 (8)	0.0262 (9)	0.0276 (9)	0.0021 (7)	0.0007 (7)	0.0091 (7)
C72	0.0211 (9)	0.0295 (9)	0.0284 (9)	0.0020 (7)	0.0023 (7)	0.0097 (7)
C73	0.0282 (10)	0.0375 (10)	0.0250 (9)	0.0010 (8)	0.0020 (8)	0.0069 (8)
N74	0.0317 (10)	0.0655 (13)	0.0382 (10)	0.0107 (9)	0.0095 (8)	0.0052 (9)
C41	0.0214 (9)	0.0229 (8)	0.0303 (9)	−0.0009 (7)	0.0017 (7)	0.0048 (7)
C42	0.0243 (9)	0.0284 (9)	0.0283 (9)	−0.0045 (7)	0.0039 (7)	0.0020 (7)
C43	0.0205 (9)	0.0290 (10)	0.0326 (10)	−0.0027 (7)	0.0045 (7)	−0.0033 (8)
N44	0.0312 (9)	0.0305 (9)	0.0494 (11)	−0.0045 (7)	0.0039 (8)	0.0034 (8)

C9	0.0317 (10)	0.0222 (9)	0.0333 (10)	0.0017 (7)	0.0063 (8)	0.0049 (7)

Geometric parameters (Å, º)

Ag1—S1	2.5074 (5)	N7—C8	1.462 (2)
Ag1—S	2.4390 (5)	N7—C71	1.465 (2)
Ag1—N4	2.5490 (14)	C8—H8A	0.9900
Ag1—N7	2.5561 (15)	C8—H8B	0.9900
C—N	1.152 (3)	C8—C9	1.528 (3)
C—S	1.670 (2)	C71—H71A	0.9900
S1—C2	1.8241 (19)	C71—H71B	0.9900
S1—C9	1.8211 (19)	C71—C72	1.541 (2)
C2—H2A	0.9900	C72—H72A	0.9900
C2—H2B	0.9900	C72—H72B	0.9900
C2—C3	1.526 (3)	C72—C73	1.467 (3)
C3—H3A	0.9900	C73—N74	1.132 (3)
C3—H3B	0.9900	C41—H41A	0.9900
C3—N4	1.468 (2)	C41—H41B	0.9900
N4—C5	1.479 (2)	C41—C42	1.548 (2)
N4—C41	1.462 (2)	C42—H42A	0.9900
C5—H5A	0.9900	C42—H42B	0.9900
C5—H5B	0.9900	C42—C43	1.464 (3)
C5—C6	1.525 (2)	C43—N44	1.135 (2)
C6—H6A	0.9900	C9—H9A	0.9900
C6—H6B	0.9900	C9—H9B	0.9900
C6—N7	1.476 (2)		

S1—Ag1—N4	79.60 (4)	C8—N7—C6	114.09 (14)
S1—Ag1—N7	79.77 (4)	C8—N7—C71	111.70 (14)
S—Ag1—S1	160.21 (2)	C71—N7—Ag1	101.89 (10)
S—Ag1—N4	119.16 (4)	C71—N7—C6	113.25 (14)
S—Ag1—N7	111.02 (4)	N7—C8—H8A	108.5
N4—Ag1—N7	71.15 (5)	N7—C8—H8B	108.5
N—C—S	177.7 (2)	N7—C8—C9	115.13 (15)
C2—S1—Ag1	95.16 (7)	H8A—C8—H8B	107.5
C9—S1—Ag1	101.15 (6)	C9—C8—H8A	108.5
C9—S1—C2	103.37 (9)	C9—C8—H8B	108.5
S1—C2—H2A	108.3	N7—C71—H71A	108.6
S1—C2—H2B	108.3	N7—C71—H71B	108.6
H2A—C2—H2B	107.4	N7—C71—C72	114.52 (14)
C3—C2—S1	115.81 (13)	H71A—C71—H71B	107.6
C3—C2—H2A	108.3	C72—C71—H71A	108.6
C3—C2—H2B	108.3	C72—C71—H71B	108.6
C—S—Ag1	97.17 (7)	C71—C72—H72A	109.5
C2—C3—H3A	108.8	C71—C72—H72B	109.5
C2—C3—H3B	108.8	H72A—C72—H72B	108.1
H3A—C3—H3B	107.7	C73—C72—C71	110.56 (15)
N4—C3—C2	113.77 (15)	C73—C72—H72A	109.5

N4—C3—H3A	108.8	C73—C72—H72B	109.5
N4—C3—H3B	108.8	N74—C73—C72	177.8 (2)
C3—N4—Ag1	110.77 (10)	N4—C41—H41A	108.7
C3—N4—C5	114.32 (14)	N4—C41—H41B	108.7
C5—N4—Ag1	102.34 (10)	N4—C41—C42	114.42 (15)
C41—N4—Ag1	103.42 (10)	H41A—C41—H41B	107.6
C41—N4—C3	112.58 (14)	C42—C41—H41A	108.7
C41—N4—C5	112.35 (14)	C42—C41—H41B	108.7
N4—C5—H5A	108.8	C41—C42—H42A	109.5
N4—C5—H5B	108.8	C41—C42—H42B	109.5
N4—C5—C6	113.72 (14)	H42A—C42—H42B	108.1
H5A—C5—H5B	107.7	C43—C42—C41	110.59 (16)
C6—C5—H5A	108.8	C43—C42—H42A	109.5
C6—C5—H5B	108.8	C43—C42—H42B	109.5
C5—C6—H6A	108.9	N44—C43—C42	178.4 (2)
C5—C6—H6B	108.9	S1—C9—H9A	108.3
H6A—C6—H6B	107.7	S1—C9—H9B	108.3
N7—C6—C5	113.24 (14)	C8—C9—S1	116.03 (14)
N7—C6—H6A	108.9	C8—C9—H9A	108.3
N7—C6—H6B	108.9	C8—C9—H9B	108.3
C6—N7—Ag1	111.38 (10)	H9A—C9—H9B	107.4
C8—N7—Ag1	103.40 (10)		

Ag1—S1—C2—C3	−52.45 (14)	N4—C41—C42—C43	−173.76 (16)
Ag1—S1—C9—C8	−18.86 (15)	C5—N4—C41—C42	−60.7 (2)
Ag1—N4—C5—C6	−58.42 (15)	C5—C6—N7—Ag1	−16.69 (18)
Ag1—N4—C41—C42	−170.34 (13)	C5—C6—N7—C8	−133.28 (16)
Ag1—N7—C8—C9	−54.08 (16)	C5—C6—N7—C71	97.45 (17)
Ag1—N7—C71—C72	−168.44 (12)	C6—N7—C8—C9	67.1 (2)
S1—C2—C3—N4	55.39 (19)	C6—N7—C71—C72	71.83 (19)
C2—S1—C9—C8	−116.97 (15)	N7—C8—C9—S1	53.5 (2)
C2—C3—N4—Ag1	−23.22 (17)	N7—C71—C72—C73	179.87 (15)
C2—C3—N4—C5	−138.19 (15)	C8—N7—C71—C72	−58.6 (2)
C2—C3—N4—C41	92.03 (18)	C71—N7—C8—C9	−162.91 (15)
C3—N4—C5—C6	61.40 (19)	C41—N4—C5—C6	−168.71 (14)
C3—N4—C41—C42	70.1 (2)	C9—S1—C2—C3	50.32 (16)
N4—C5—C6—N7	54.1 (2)		

μ-Thiocyanato-κ^2S:S-bis{[7-(2-cyanoethyl)-1,4-dithia-7-azacyclononane-κ^3N,S,S']silver(I)} tetrafluoridoborate (Ag2L32mu-SCNBF4)

Crystal data

$[Ag_2(C_9H_{16}N_2S_2)_2(SCN)]BF_4$
M_r = 793.34
Monoclinic, $C2/c$
a = 28.537 (3) Å
b = 8.4362 (11) Å
c = 27.216 (3) Å
β = 119.940 (9)°

V = 5677.6 (12) Å^3
Z = 8
F(000) = 3168
D_x = 1.856 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 35 reflections
θ = 11.1–15.4°

μ = 1.79 mm^{-1}
T = 150 K

Tablet, colourless
0.27 × 0.15 × 0.12 mm

Data collection

Stoe STADI4 4-circle diffractometer
Radiation source: fine-focus sealed tube
Planar graphite monochromator
Scan width (ω) = 1.04 – 1.20, scan ratio $2\theta:\omega$ = 1.00 I(Net) and sigma(I) calculated according to Blessing (1987)
Absorption correction: integration (SHELXTL; Sheldrick, 2008)
$T_{\min}$ = 0.713, $T_{\max}$ = 0.822

5547 measured reflections
4972 independent reflections
4138 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
$\theta_{\max}$ = 25.0°, $\theta_{\min}$ = 2.6°
$h = -33 \rightarrow 33$
$k = -10 \rightarrow 0$
$l = -32 \rightarrow 32$
3 standard reflections every 60 min
intensity decay: 7.0%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.075
S = 1.15
4972 reflections
326 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
$w = 1/[\sigma^2(F_o^2) + (0.015P)^2 + 34.6966P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.56 e Å^{-3}
$\Delta\rho_{\min}$ = −0.52 e Å^{-3}
Extinction correction: SHELXL2018 (Sheldrick, 2015), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.000099 (18)

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	$U_{\text{iso}}*/U_{\text{eq}}$
Ag1	0.08025 (2)	0.93692 (4)	0.41389 (2)	0.02154 (11)
Ag2	0.09609 (2)	0.98647 (5)	0.31130 (2)	0.02240 (11)
S1A	0.04351 (5)	0.82782 (15)	0.22085 (5)	0.0216 (3)
S4A	0.16145 (5)	0.74507 (15)	0.35120 (5)	0.0200 (3)
S4	0.02877 (5)	0.87553 (15)	0.46833 (5)	0.0215 (3)
S1	0.07752 (5)	0.63126 (14)	0.40150 (5)	0.0189 (3)
S	0.08733 (5)	1.18937 (14)	0.37032 (5)	0.0210 (3)
F1	0.33209 (13)	1.0994 (4)	0.31883 (13)	0.0432 (9)
C8A	0.11625 (18)	1.0142 (6)	0.20333 (19)	0.0210 (11)
H8AA	0.137024	1.020249	0.183166	0.025*
H8AB	0.092061	1.107647	0.192029	0.025*
F2	0.32206 (13)	1.0454 (4)	0.39447 (15)	0.0442 (9)
C	0.0214 (2)	1.2361 (6)	0.3298 (2)	0.0244 (12)
F4	0.39578 (15)	0.9572 (5)	0.39134 (17)	0.0588 (11)

N7A	0.15398 (14)	1.0213 (4)	0.26449 (16)	0.0164 (8)
F3	0.38643 (15)	1.2183 (4)	0.40266 (15)	0.0518 (10)
C6	0.14043 (18)	0.8308 (6)	0.54970 (19)	0.0178 (10)
H6A	0.169613	0.866183	0.587338	0.021*
H6B	0.135847	0.715265	0.552039	0.021*
C72A	0.2050 (2)	1.2596 (6)	0.2569 (2)	0.0234 (11)
H72A	0.228958	1.180650	0.253513	0.028*
H72B	0.178893	1.298119	0.218369	0.028*
C9	0.13812 (19)	0.5770 (6)	0.46780 (19)	0.0201 (10)
H9A	0.127040	0.538570	0.494868	0.024*
H9B	0.156343	0.488275	0.460250	0.024*
N7	0.15811 (15)	0.8593 (4)	0.50755 (16)	0.0154 (8)
C5	0.08767 (18)	0.9137 (6)	0.5373 (2)	0.0225 (11)
H5A	0.094240	1.029496	0.541132	0.027*
H5B	0.078955	0.881427	0.566835	0.027*
C3A	0.12826 (19)	0.6089 (6)	0.2919 (2)	0.0231 (11)
H3AA	0.145843	0.618064	0.268501	0.028*
H3AB	0.134308	0.499488	0.306949	0.028*
N74A	0.26226 (18)	1.4920 (5)	0.32126 (19)	0.0292 (10)
N74	0.26658 (19)	1.3362 (6)	0.56519 (19)	0.0342 (11)
C3	0.0239 (2)	0.6604 (6)	0.4664 (2)	0.0226 (11)
H3A	0.054530	0.618100	0.501832	0.027*
H3B	−0.009822	0.630655	0.466159	0.027*
C72	0.1858 (2)	1.1416 (6)	0.5362 (2)	0.0234 (11)
H72C	0.153835	1.177628	0.500623	0.028*
H72D	0.175752	1.138219	0.566178	0.028*
C6A	0.19758 (18)	0.9034 (6)	0.28424 (19)	0.0178 (10)
H6AA	0.229408	0.953201	0.285137	0.021*
H6AB	0.185532	0.815320	0.256543	0.021*
C71	0.20226 (18)	0.9769 (6)	0.5278 (2)	0.0207 (11)
H71A	0.215047	0.983506	0.500082	0.025*
H71B	0.232883	0.939793	0.564235	0.025*
C8	0.17881 (18)	0.7127 (6)	0.4957 (2)	0.0201 (11)
H8A	0.209173	0.673261	0.531875	0.024*
H8B	0.193690	0.739896	0.470763	0.024*
N	−0.02324 (19)	1.2731 (6)	0.3034 (2)	0.0405 (13)
C5A	0.21473 (18)	0.8355 (6)	0.3426 (2)	0.0208 (11)
H5AA	0.231275	0.921751	0.370783	0.025*
H5AB	0.243103	0.754923	0.351521	0.025*
C9A	0.08164 (19)	0.8633 (6)	0.1847 (2)	0.0229 (11)
H9AA	0.105591	0.771253	0.191253	0.027*
H9AB	0.055960	0.869820	0.143422	0.027*
C2A	0.06761 (19)	0.6337 (6)	0.2535 (2)	0.0244 (11)
H2AA	0.049892	0.609113	0.275916	0.029*
H2AB	0.054699	0.554352	0.222610	0.029*
C73A	0.23715 (19)	1.3917 (6)	0.2920 (2)	0.0194 (11)
C73	0.2306 (2)	1.2535 (6)	0.5525 (2)	0.0239 (11)
B1	0.3592 (2)	1.0805 (7)	0.3769 (2)	0.0235 (13)

C2	0.02391 (19)	0.5797 (6)	0.4164 (2)	0.0221 (11)
H2A	−0.011122	0.602855	0.381983	0.027*
H2B	0.025409	0.463750	0.422692	0.027*
C71A	0.17420 (19)	1.1811 (6)	0.2842 (2)	0.0189 (10)
H71C	0.198667	1.177462	0.325824	0.023*
H71D	0.143187	1.249674	0.276836	0.023*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.0239 (2)	0.0180 (2)	0.0196 (2)	0.00354 (16)	0.00846 (16)	0.00433 (16)
Ag2	0.0245 (2)	0.0204 (2)	0.0276 (2)	−0.00087 (16)	0.01692 (17)	−0.00617 (17)
S1A	0.0141 (6)	0.0252 (7)	0.0230 (6)	−0.0016 (5)	0.0075 (5)	−0.0031 (5)
S4A	0.0210 (6)	0.0194 (6)	0.0204 (6)	0.0003 (5)	0.0108 (5)	0.0021 (5)
S4	0.0164 (6)	0.0248 (7)	0.0211 (6)	0.0004 (5)	0.0076 (5)	−0.0045 (5)
S1	0.0201 (6)	0.0171 (6)	0.0170 (6)	0.0003 (5)	0.0074 (5)	−0.0011 (5)
S	0.0257 (6)	0.0147 (6)	0.0216 (6)	0.0015 (5)	0.0110 (5)	−0.0020 (5)
F1	0.046 (2)	0.049 (2)	0.0232 (16)	−0.0090 (17)	0.0084 (15)	0.0060 (15)
C8A	0.019 (2)	0.025 (3)	0.017 (2)	0.001 (2)	0.008 (2)	0.002 (2)
F2	0.0427 (19)	0.047 (2)	0.058 (2)	−0.0115 (17)	0.0365 (18)	−0.0007 (18)
C	0.037 (3)	0.012 (3)	0.032 (3)	0.003 (2)	0.023 (3)	0.001 (2)
F4	0.049 (2)	0.058 (3)	0.073 (3)	0.021 (2)	0.034 (2)	0.025 (2)
N7A	0.0141 (19)	0.011 (2)	0.019 (2)	0.0033 (16)	0.0050 (16)	0.0016 (16)
F3	0.059 (2)	0.056 (2)	0.051 (2)	−0.033 (2)	0.0348 (19)	−0.0278 (19)
C6	0.017 (2)	0.021 (3)	0.013 (2)	−0.001 (2)	0.0061 (19)	−0.001 (2)
C72A	0.031 (3)	0.018 (3)	0.025 (3)	−0.007 (2)	0.017 (2)	−0.006 (2)
C9	0.024 (3)	0.011 (2)	0.018 (2)	0.007 (2)	0.006 (2)	0.003 (2)
N7	0.0156 (19)	0.012 (2)	0.017 (2)	−0.0005 (16)	0.0068 (16)	0.0001 (16)
C5	0.019 (2)	0.030 (3)	0.021 (3)	−0.003 (2)	0.011 (2)	−0.011 (2)
C3A	0.022 (3)	0.015 (3)	0.034 (3)	−0.002 (2)	0.016 (2)	−0.002 (2)
N74A	0.032 (2)	0.026 (3)	0.030 (2)	−0.007 (2)	0.016 (2)	−0.006 (2)
N74	0.041 (3)	0.032 (3)	0.033 (3)	−0.012 (2)	0.021 (2)	−0.012 (2)
C3	0.020 (3)	0.023 (3)	0.024 (3)	−0.003 (2)	0.011 (2)	0.000 (2)
C72	0.028 (3)	0.015 (3)	0.024 (3)	−0.005 (2)	0.011 (2)	−0.003 (2)
C6A	0.016 (2)	0.019 (3)	0.020 (2)	0.000 (2)	0.010 (2)	−0.002 (2)
C71	0.018 (2)	0.023 (3)	0.019 (2)	−0.004 (2)	0.008 (2)	0.001 (2)
C8	0.019 (2)	0.018 (3)	0.021 (3)	0.006 (2)	0.008 (2)	0.004 (2)
N	0.034 (3)	0.029 (3)	0.061 (3)	0.010 (2)	0.025 (3)	0.014 (3)
C5A	0.017 (2)	0.018 (3)	0.022 (3)	0.000 (2)	0.006 (2)	−0.002 (2)
C9A	0.023 (3)	0.027 (3)	0.016 (2)	−0.001 (2)	0.007 (2)	−0.003 (2)
C2A	0.024 (3)	0.020 (3)	0.030 (3)	−0.007 (2)	0.014 (2)	−0.003 (2)
C73A	0.019 (2)	0.019 (3)	0.026 (3)	0.002 (2)	0.015 (2)	0.001 (2)
C73	0.033 (3)	0.021 (3)	0.017 (3)	−0.002 (2)	0.012 (2)	−0.003 (2)
B1	0.018 (3)	0.024 (3)	0.024 (3)	−0.003 (2)	0.007 (2)	−0.001 (3)
C2	0.021 (2)	0.015 (3)	0.025 (3)	−0.002 (2)	0.008 (2)	0.000 (2)
C71A	0.021 (2)	0.016 (3)	0.020 (2)	−0.003 (2)	0.010 (2)	−0.004 (2)

Geometric parameters (Å, º)

Ag1—Ag2	3.0716 (6)	C9—H9A	0.9900
Ag1—S4	2.6065 (13)	C9—H9B	0.9900
Ag1—S1	2.5966 (13)	C9—C8	1.535 (7)
Ag1—S	2.4943 (13)	N7—C71	1.477 (6)
Ag1—N7	2.492 (4)	N7—C8	1.474 (6)
Ag2—S1A	2.5329 (13)	C5—H5A	0.9900
Ag2—S4A	2.6046 (13)	C5—H5B	0.9900
Ag2—S	2.4441 (13)	C3A—H3AA	0.9900
Ag2—N7A	2.557 (4)	C3A—H3AB	0.9900
S1A—C9A	1.819 (5)	C3A—C2A	1.525 (7)
S1A—C2A	1.826 (5)	N74A—C73A	1.137 (6)
S4A—C3A	1.816 (5)	N74—C73	1.142 (6)
S4A—C5A	1.818 (5)	C3—H3A	0.9900
S4—C5	1.818 (5)	C3—H3B	0.9900
S4—C3	1.819 (5)	C3—C2	1.523 (7)
S1—C9	1.828 (5)	C72—H72C	0.9900
S1—C2	1.820 (5)	C72—H72D	0.9900
S—C	1.685 (5)	C72—C71	1.520 (7)
F1—B1	1.379 (6)	C72—C73	1.470 (7)
C8A—H8AA	0.9900	C6A—H6AA	0.9900
C8A—H8AB	0.9900	C6A—H6AB	0.9900
C8A—N7A	1.464 (6)	C6A—C5A	1.520 (6)
C8A—C9A	1.534 (7)	C71—H71A	0.9900
F2—B1	1.395 (7)	C71—H71B	0.9900
C—N	1.151 (7)	C8—H8A	0.9900
F4—B1	1.384 (7)	C8—H8B	0.9900
N7A—C6A	1.469 (6)	C5A—H5AA	0.9900
N7A—C71A	1.460 (6)	C5A—H5AB	0.9900
F3—B1	1.380 (7)	C9A—H9AA	0.9900
C6—H6A	0.9900	C9A—H9AB	0.9900
C6—H6B	0.9900	C2A—H2AA	0.9900
C6—N7	1.485 (6)	C2A—H2AB	0.9900
C6—C5	1.537 (6)	C2—H2A	0.9900
C72A—H72A	0.9900	C2—H2B	0.9900
C72A—H72B	0.9900	C71A—H71C	0.9900
C72A—C73A	1.457 (7)	C71A—H71D	0.9900
C72A—C71A	1.556 (6)		

S4—Ag1—Ag2	157.53 (3)	C6—C5—H5B	108.2
S1—Ag1—Ag2	91.47 (3)	H5A—C5—H5B	107.3
S1—Ag1—S4	83.55 (4)	S4A—C3A—H3AA	108.4
S—Ag1—Ag2	50.81 (3)	S4A—C3A—H3AB	108.4
S—Ag1—S4	129.95 (4)	H3AA—C3A—H3AB	107.4
S—Ag1—S1	142.23 (4)	C2A—C3A—S4A	115.6 (3)
N7—Ag1—Ag2	120.33 (9)	C2A—C3A—H3AA	108.4
N7—Ag1—S4	80.45 (9)	C2A—C3A—H3AB	108.4

N7—Ag1—S1	79.96 (9)	S4—C3—H3A	108.3
N7—Ag1—S	117.91 (9)	S4—C3—H3B	108.3
S1A—Ag2—Ag1	121.80 (3)	H3A—C3—H3B	107.4
S1A—Ag2—S4A	86.88 (4)	C2—C3—S4	115.9 (4)
S1A—Ag2—N7A	78.06 (9)	C2—C3—H3A	108.3
S4A—Ag2—Ag1	85.08 (3)	C2—C3—H3B	108.3
S—Ag2—Ag1	52.28 (3)	H72C—C72—H72D	108.2
S—Ag2—S1A	143.47 (4)	C71—C72—H72C	109.6
S—Ag2—S4A	124.09 (4)	C71—C72—H72D	109.6
S—Ag2—N7A	123.39 (9)	C73—C72—H72C	109.6
N7A—Ag2—Ag1	153.28 (8)	C73—C72—H72D	109.6
N7A—Ag2—S4A	77.95 (9)	C73—C72—C71	110.1 (4)
C9A—S1A—Ag2	102.39 (16)	N7A—C6A—H6AA	108.7
C9A—S1A—C2A	103.2 (2)	N7A—C6A—H6AB	108.7
C2A—S1A—Ag2	96.01 (17)	N7A—C6A—C5A	114.2 (4)
C3A—S4A—Ag2	100.17 (16)	H6AA—C6A—H6AB	107.6
C3A—S4A—C5A	104.4 (2)	C5A—C6A—H6AA	108.7
C5A—S4A—Ag2	95.11 (16)	C5A—C6A—H6AB	108.7
C5—S4—Ag1	93.39 (16)	N7—C71—C72	113.5 (4)
C5—S4—C3	103.0 (2)	N7—C71—H71A	108.9
C3—S4—Ag1	103.85 (17)	N7—C71—H71B	108.9
C9—S1—Ag1	99.68 (16)	C72—C71—H71A	108.9
C2—S1—Ag1	100.52 (16)	C72—C71—H71B	108.9
C2—S1—C9	101.9 (2)	H71A—C71—H71B	107.7
Ag2—S—Ag1	76.91 (4)	C9—C8—H8A	108.2
C—S—Ag1	100.51 (18)	C9—C8—H8B	108.2
C—S—Ag2	100.38 (18)	N7—C8—C9	116.6 (4)
H8AA—C8A—H8AB	107.7	N7—C8—H8A	108.2
N7A—C8A—H8AA	108.9	N7—C8—H8B	108.2
N7A—C8A—H8AB	108.9	H8A—C8—H8B	107.3
N7A—C8A—C9A	113.3 (4)	S4A—C5A—H5AA	108.3
C9A—C8A—H8AA	108.9	S4A—C5A—H5AB	108.3
C9A—C8A—H8AB	108.9	C6A—C5A—S4A	116.0 (3)
N—C—S	177.3 (5)	C6A—C5A—H5AA	108.3
C8A—N7A—Ag2	105.7 (3)	C6A—C5A—H5AB	108.3
C8A—N7A—C6A	113.4 (4)	H5AA—C5A—H5AB	107.4
C6A—N7A—Ag2	112.3 (3)	S1A—C9A—H9AA	108.6
C71A—N7A—Ag2	99.1 (3)	S1A—C9A—H9AB	108.6
C71A—N7A—C8A	112.8 (4)	C8A—C9A—S1A	114.7 (3)
C71A—N7A—C6A	112.6 (4)	C8A—C9A—H9AA	108.6
H6A—C6—H6B	107.5	C8A—C9A—H9AB	108.6
N7—C6—H6A	108.4	H9AA—C9A—H9AB	107.6
N7—C6—H6B	108.4	S1A—C2A—H2AA	107.7
N7—C6—C5	115.5 (4)	S1A—C2A—H2AB	107.7
C5—C6—H6A	108.4	C3A—C2A—S1A	118.6 (3)
C5—C6—H6B	108.4	C3A—C2A—H2AA	107.7
H72A—C72A—H72B	108.2	C3A—C2A—H2AB	107.7
C73A—C72A—H72A	109.8	H2AA—C2A—H2AB	107.1

C73A—C72A—H72B	109.8	N74A—C73A—C72A	177.3 (5)
C73A—C72A—C71A	109.4 (4)	N74—C73—C72	177.7 (6)
C71A—C72A—H72A	109.8	F1—B1—F2	109.2 (4)
C71A—C72A—H72B	109.8	F1—B1—F4	108.9 (5)
S1—C9—H9A	108.7	F1—B1—F3	109.6 (5)
S1—C9—H9B	108.7	F4—B1—F2	109.8 (5)
H9A—C9—H9B	107.6	F3—B1—F2	109.6 (5)
C8—C9—S1	114.3 (3)	F3—B1—F4	109.6 (4)
C8—C9—H9A	108.7	S1—C2—H2A	107.8
C8—C9—H9B	108.7	S1—C2—H2B	107.8
C6—N7—Ag1	111.1 (3)	C3—C2—S1	117.9 (3)
C71—N7—Ag1	111.4 (3)	C3—C2—H2A	107.8
C71—N7—C6	112.1 (4)	C3—C2—H2B	107.8
C8—N7—Ag1	104.3 (3)	H2A—C2—H2B	107.2
C8—N7—C6	111.2 (4)	N7A—C71A—C72A	115.5 (4)
C8—N7—C71	106.5 (3)	N7A—C71A—H71C	108.4
S4—C5—H5A	108.2	N7A—C71A—H71D	108.4
S4—C5—H5B	108.2	C72A—C71A—H71C	108.4
C6—C5—S4	116.4 (3)	C72A—C71A—H71D	108.4
C6—C5—H5A	108.2	H71C—C71A—H71D	107.5

Ag1—S4—C5—C6	−49.6 (4)	C9—S1—C2—C3	59.1 (4)
Ag1—S4—C3—C2	−27.3 (4)	N7—C6—C5—S4	54.9 (5)
Ag1—S1—C9—C8	−20.8 (4)	C5—S4—C3—C2	−124.1 (4)
Ag1—S1—C2—C3	−43.3 (4)	C5—C6—N7—Ag1	−23.3 (5)
Ag1—N7—C71—C72	60.8 (4)	C5—C6—N7—C71	102.0 (4)
Ag1—N7—C8—C9	−55.7 (4)	C5—C6—N7—C8	−138.9 (4)
Ag2—S1A—C9A—C8A	−22.3 (4)	C3A—S4A—C5A—C6A	50.6 (4)
Ag2—S1A—C2A—C3A	−49.9 (4)	C3—S4—C5—C6	55.5 (4)
Ag2—S4A—C3A—C2A	−25.5 (4)	C6A—N7A—C71A—C72A	70.4 (5)
Ag2—S4A—C5A—C6A	−51.3 (4)	C71—N7—C8—C9	−173.6 (4)
Ag2—N7A—C6A—C5A	−24.6 (5)	C8—N7—C71—C72	173.9 (4)
Ag2—N7A—C71A—C72A	−170.8 (3)	C5A—S4A—C3A—C2A	−123.6 (4)
S4A—C3A—C2A—S1A	56.3 (5)	C9A—S1A—C2A—C3A	54.4 (4)
S4—C3—C2—S1	51.2 (5)	C9A—C8A—N7A—Ag2	−55.0 (4)
S1—C9—C8—N7	55.5 (5)	C9A—C8A—N7A—C6A	68.4 (5)
C8A—N7A—C6A—C5A	−144.3 (4)	C9A—C8A—N7A—C71A	−162.2 (4)
C8A—N7A—C71A—C72A	−59.5 (5)	C2A—S1A—C9A—C8A	−121.6 (4)
N7A—C8A—C9A—S1A	55.3 (5)	C73A—C72A—C71A—N7A	−161.9 (4)
N7A—C6A—C5A—S4A	56.0 (5)	C73—C72—C71—N7	−176.1 (4)
C6—N7—C71—C72	−64.3 (5)	C2—S1—C9—C8	−123.8 (4)
C6—N7—C8—C9	64.0 (5)	C71A—N7A—C6A—C5A	86.2 (5)