Coordination chemistry of nitrile-functionalized mixed thia-aza macrocycles [9]aneN₂S and [9]aneNS₂ towards silver(I)

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The coordination chemistry towards silver(I) of the small-ring macrocycles [9]aneN₂S (1-thia-4,7-diazacyclononane) and [9]aneNS₂ (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-κN,N',S]silver(I) tetrafluoridoborate, [Ag(C₁₀H₁₆N₄S₂)₂]BF₄ or [Ag(L₁)₂]BF₄, [4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane-κN,N',S](thiocyanato-κS)-silver(I), [Ag(C₁₂H₂₀N₄S)(NCS)] or [Ag(L²)(SCN)], and μ-thiocyanato-κS,S-bis[7-(2-cyanoethyl)-1,4-dithia-7-azacyclononane-κN,N',S,S']silver(I) tetrafluoridoborate, [Ag₂(C₆H₆N₄S₂)₂(SCN)]BF₄ or [Ag₂(L³)₂(μ-SCN)]BF₄, 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 polymeric 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 [L₁ = 4,7-bis(cyanomethyl)-1-thia-4,7-diazacyclononane, L² = 4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane and L³ = 7-(2-cyanoethyl)-1,4-dithia-7-azacyclononanone] 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 [Ag₂(μ₂-κCN)(L₁)₂]BF₄·MeCN, featuring a side-on two-electron (σ) μ₂-κC₉C₉C bridging cyanide, was isolated from the reaction of L₁, AgBF₄ and iBu₄NCN in a 1:1:0.5 molar ratio, the com-
plexes \([\text{Ag}_2(\text{L}_2^2)(\mu-\text{CN})]\text{BF}_4\) and \([\text{Ag}_2(\text{L}_3^3)(\mu-\text{CN})]\text{BF}_4\), exhibiting a \(\text{CN}^{-}\) ligand bridging two metal centres in a linear four-electron \((\sigma + \pi)\) \(\mu_2-\kappa\text{C}2\text{C}N\) manner (Vahrenkamp et al., 1997), were isolated starting from \(\text{L}_2^3\) and \(\text{L}_3^3\), respectively, under the same experimental conditions (Lippolis et al., 1999).

\([\text{Ag}_2(\text{L}_3^3)(\mu-\text{SCN})]\text{BF}_4\), MeCN was the first discrete binuclear complex, and is still the only one reported in the literature, featuring a pure two-electron \((\sigma)\) \(\mu_2-\kappa\text{C}2\text{C}N\) 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 \(\text{L}_1\) as compared to \(\text{L}_2\) would allow a closer approach of two \([\text{Ag}(\text{L}_3^3)]^+\) 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 \([9\text{aneN}_2\text{S}] (1\text{-thia}-4,7\text{-diazacyclononane})\) and \([9\text{aneNS}_2] (1,4\text{-dithia}-7\text{-azacyclononane})\) in determining the coordination chemistry towards silver(I) both in the absence or in the presence of exogenous bridging ligands.

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 (\(\text{L}_1\)), 4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane (\(\text{L}_2\)) and 7-(2-cyanoethyl)-1,4-dithia-7-azacyclononane (\(\text{L}_3\)) 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 \(\text{L}_2\) and \(\text{L}_3\) with silver(I) in the presence of thiocyanate, namely, an \(\text{L}/\text{Ag}^+/\text{SCN}^{-}\) 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.

2.2.1. Synthesis of \([\text{Ag}(\text{L}_2^3)]\text{BF}_4\). A mixture of 4,7-bis(cyanomethyl)-1-thia-4,7-diazacyclononane (\(\text{L}_1\)) (20 mg, 0.089 mmol) and \(\text{AgBF}_4\) (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\(_2\)O 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 \([\text{Ag}(\text{L}_2^3)]\text{BF}_4\), C\(_{20}\)H\(_32\)AgO\(_4\)S\(_2\): C 50.38, H 4.22, N 9.04; found: C 50.45, H 4.20, N 8.99. FAB mass spectrum (3-NOBA) \(m/z\): 555 and 331 for \([^{107}\text{Ag}(\text{L}_2^3)]^+\) and \([^{109}\text{Ag}(\text{L}_2^3)]^+\), respectively. IR spectrum (KBr disc) \(\nu (\text{cm}^{-1})\): 2928 (\(\nu\)), 2833 (\(\nu\)), 2243 (\(\nu\)) for \(\text{CN}\) stretch in \(\text{L}_1\), 1452 (\(\nu\)), 1335 (\(\nu\)), 1223 (\(\nu\)), 1109 (\(\nu\)), 998 (\(\nu\)), 920 (\(\nu\)), 878 (\(\nu\)).

2.2.2. Synthesis of \([\text{Ag}(\text{L}_3^3)]\text{SCN}\)]. A mixture of 4,7-bis(cyanoethyl)-1-thia-4,7-diazacyclononane (\(\text{L}_3\)) (21.7 mg, 0.086 mmol) and \(\text{AgBF}_4\) (16.74 mg, 0.086 mmol) in MeCN (3 ml) was stirred in the dark at room temperature for 30 min. A solution of \(\text{Bu}_4\text{NSCN}\) (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\(_2\)O vapour into the remaining solution (yield 10.5 mg; 58%; m.p. 135 °C, with decomposi-
Experimental details.

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

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>[Ag(L^1)]BF_4</th>
<th>[Ag(L^2)(SCN)]</th>
<th>[Ag(L^3)_{2}(μ-SCN)]BF_4</th>
</tr>
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<tbody>
<tr>
<td>Chemical formula</td>
<td>[Ag(C_{10}H_{16}N_{4}S)_{2}]BF_4</td>
<td>[Ag(C_{10}H_{16}N_{4}S)(NCS)]</td>
<td>[Ag(C_{12}H_{20}N_{4}S)(NCS)]_{2}</td>
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<tr>
<td>M_0</td>
<td>643.33</td>
<td>418.33</td>
<td>793.34</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic, P</td>
<td>Triclinic, P</td>
<td>Monoclinic, C2/c</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
<td>10.1813 (6), 10.2237 (6), 15.0154 (9)</td>
<td>8.4426 (6), 8.5739 (6), 11.8497 (8)</td>
<td>28.537 (3), 8.4362 (11), 27.216 (3)</td>
</tr>
<tr>
<td>α, β, γ (°)</td>
<td>73.446 (2), 82.398 (2), 61.781 (2)</td>
<td>96.585 (1), 99.023 (1), 95.313 (1)</td>
<td>90, 119.940 (9), 90</td>
</tr>
<tr>
<td>V (Å^3)</td>
<td>1320.11 (14)</td>
<td>836.19 (1)</td>
<td>5677.6 (12)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>0.98</td>
<td>1.46</td>
<td>1.79</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.3 × 0.2 × 0.14</td>
<td>0.36 × 0.30 × 0.07</td>
<td>0.27 × 0.15 × 0.12</td>
</tr>
</tbody>
</table>

| 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 > 2σ(I)] reflections | 13703, 6151, 5420 | 5159, 3668, 3401 | 5547, 4972, 4138 |
| R_{int} | 0.035 | 0.022 | 0.025 |
| (sin θ/λ)_{max} (Å⁻¹) | 0.679 | 0.675 | 0.594 |

Refinement

R[F^2 > 2σ(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 |
| Δρ_{max}, Δρ_{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).

2.2.3. Synthesis of [Ag_2(L^3)_2(μ-SCN)]BF_4. A mixture of 7-(2-cyanoethyl)-1,4-dithia-7-azacyclononane (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 Bu_4NSCN (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_3O vapour into the remaining solution (yield 18.3 mg; 46%; m.p. 140–142 °C). Analysis calculated (%) for [Ag_2(L^3)_2(μ-SCN)]BF_4: 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 [107Ag(L^3)^+]. IR spectrum (KBr disc) ν (cm⁻¹): 2911 (m), 2826 (m), 2246 (m) (ν_{CN} stretch in 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(L^1)]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 $U_{iso}(H) = 1.2U_{eq}(C)$.

3. Results and discussion

Following the synthetic strategy adopted in previous studies to favour the formation of inorganic polymers, we reacted $L_1$ 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$_2$O vapour into the remaining solution. A single-crystal X-ray structure determination confirmed the product to be the discrete mononuclear Ag$^1$ homoleptic complex [Ag($L_1$)$_2$]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$_3$SO$_3$)$_2$ [2.696 (2)–2.753 (1) Å; [9]aneS$_3$ = 1,4,7-thiaacyclononane] (Blower et al., 1989).

The extended structure of [Ag($L_1$)$_2$]BF$_4$ features C—H···F and C—H···N 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 research papers).
supporting information) and crosslink these chains to form layers.

The formation of the mononuclear sandwich complex $[\text{Ag(L}_1^2]\text{BF}_4$ upon reaction of $\text{L}_1$ 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 $\text{L}_2$ with $\text{AgBF}_4$ afforded the binuclear complex $[\text{Ag}_2(\text{L}_2^2)\text{[(BF}_4]^2$, in which two inversion-related $[\text{Ag}(\text{L}_2^2)]^+$ 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 $[\text{Ag}(\text{L}_3)]\text{BF}_4$, in which each AgI ion of the $[\text{Ag}(\text{L}_3)]^+$ repeating unit is bound by the $[9\text{aneN}_2\text{S}]$ macrocyclic moiety of the ligand and by the nitrile group of a symmetry-related $[\text{Ag}(\text{L}_3)]^+$ 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–$ and Ag–N and Ag–S distances $[\text{Ag}–\text{N} = 2.414 (5) \text{\ and \ Ag}–\text{S} = 2.629 (2) \text{\ A}]$ are significantly shorter and longer, respectively, than those observed in $[\text{Ag}(\text{L}_2^2)\text{SCN}]$ and in $[\text{Ag}(\text{Me}_3[9\text{aneN}_3]\text{SCN})]$ (Stockheim et al., 1991). The Ag–N distances in $[\text{Ag}(\text{Me}_3[9\text{aneN}_3]\text{SCN})]$ are comparable with those in $[\text{Ag}(\text{L}_2^2)\text{SCN}]$. As observed in $[\text{Ag}(\text{Me}_3[9\text{aneN}_3]\text{SCN})]$, the structure of $[\text{Ag}(\text{L}_2^2)\text{SCN}]$ 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···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

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**Figure 4**
View of a pair of $[\text{Ag(L}_1^2)\text{SCN}]$ molecules, showing intermolecular Ag···S interactions. H atoms have been omitted for clarity. [Symmetry code: (′) $-x + 1, -y + 1, -z + 1$.]

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**Figure 5**
Partial view, approximatively along the $a$ axis, of a chain of pairs of $[\text{Ag(L}_2^2)\text{SCN}]$ molecules linked via C—H···N(nitrile) interactions.
coordinate the metal centre in terminal rather than in bridging mode. Furthermore, pairs of \([\text{Ag}(L^2)\text{(SCN)}]\) complex units are linked into chains of molecules by \(C42-H42\cdots S\) interactions [\(N74\cdots H42A = 2.34\ \text{Å}\) and \(C42-H42A\cdots N74 = 157^\circ\); symmetry code: \((-x+1, -y+1, -z)\) (Fig. 5)]. These chains run parallel to the \(c\) axis. The \(C-H\cdot\cdot\cdot N(\text{nitrile})\) interactions are supported by \(C-\cdots H\cdot\cdot\cdot N(\text{thiocyanate})\) interactions (not shown for clarity in Fig. 5) \([C72-H72A\cdots N^i, N^i\cdots H72A = 2.51\ \text{Å}\) and \(C72-H72A\cdots N^i = 142^\circ\); see Table S2 in the supporting information for short contacts in the structure).

Surprisingly, the reaction of \(L^3\) with \(\text{AgBF}_4\) and \(\text{Bu}_4\text{NSCN}\) under the same experimental conditions used for \([\text{Ag}(L^2)\text{(SCN)}]\) afforded the binuclear complex \([\text{Ag}_2(L^3)_2(\mu-\text{SCN})]\) \[\text{BF}_4\], which shows a \(\mu_2-K\text{S}_{\text{ax}}\text{S}\) bridging \(\text{CN}^-\) ligand acting as a \(\sigma\) two-electron donor between two metal centres of \([\text{Ag}(L^3)]^+\) complex cationic units \([\text{Ag}1-S = 2.4943\ (13)\) and \(\text{Ag}2-S = 2.4441\ (13)\) Å\] (Fig. 6).

The structure is very similar to that observed for the \([\text{Ag}_2(L^3)_2(\mu-\text{CN})]\) complex cation except that \(L^1\) (which has two \(-\text{CH}_2\text{CN}\) pendant arms) and \(\text{CN}^-\) are replaced by \(L^3\) (which has only one \(-\text{CH}_2\text{CH}_2\text{CN}\) pendant arm) and \(\text{NCS}^-\). The \(\text{Ag}1-S-\text{Ag}2\) angle of 76.91 (4)\(^\circ\) is slightly smaller than the angle at the side-on bridging cyanide \([\text{Ag}1-C-\text{Ag}2 = 79.5\ (3)\) \] in \([\text{Ag}_2(L^1)_2(\mu-\text{CN})]\)\] (Lippolis et al., 1999), with the \(\text{Ag}-\text{Ag}\) distance being significantly longer [3.0716 (6) Å\] compared to the value of 2.7557 (10) Å in \([\text{Ag}_2(L^3)_2(\mu-\text{CN})]\); this could be a consequence of the longer \(\text{Ag}-\text{S}\) distances compared to \(\text{Ag}-\text{C}\) [2.153 (8) and 2.155 (8) Å, respectively]. The packing in \([\text{Ag}_2(L^3)_2(\mu-\text{SCN})]\) \(\text{BF}_4\) is a 3D network built up by an array of \(C-H\cdots N, C-H\cdots F, C-H\cdots S\) interactions (see Fig. S3 and Table S3 in the supporting information).

The complex cation \([\text{Ag}_2(L^3)_2(\mu-\text{SCN})]^+\) represents the first discrete binuclear silver(I) complex featuring a two-electron \((\sigma)\) \(\mu_2-K\text{S}_{\text{ax}}\text{S}\) bridging \(\text{SCN}^-\). A similar coordination mode of \(\text{SCN}^-\) in discrete binuclear complexes has only been observed in the complex anion \([\text{Hg}_2(\text{SCN})_7]^3^-\) in \([\text{Co}(\text{NH}_3)_{6}][\text{Hg}_2(\text{SCN})_7]\) (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 (\(\text{NCS}^-\)). The results obtained, as compared to those previously reported in the presence of cyanate (\(\text{CN}^-\)), 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 \(\text{CN}^-\) or \(\text{NCS}^-\) forming a side-on two-electron \((\sigma)\) bridge rather than a linear four-electron \((\sigma + \pi)\) one between two \([\text{Ag}(L)]^+\) units, provided the appropriate pseudo-halide is used, i.e. steric factors appear not to be responsible for the fact that \(\text{CN}^-\) shows a linear \(\mu_2-K\text{C}_{\text{ax}}\text{K}\) bridging mode in \([\text{Ag}_2(L^3)_2(\mu-\text{CN})]\) \(\text{BF}_4\), whereas \(\text{NCS}^-\) forms a side-on \(\mu_2-K\text{S}_{\text{ax}}\text{S}\) bridge in the binuclear complex \([\text{Ag}_2(L^3)_2(\mu-\text{SCN})]\) \(\text{BF}_4\). In fact, steric factors cannot be considered solely responsible for this because an end-on \(\mu_2-K\text{S}_{\text{ax}}\text{S}\) bridging mode for \(\text{NCS}^-\) would have allowed the two \([\text{Ag}(L)]^+\) units to dispose themselves further apart than in the case of \([\text{Ag}_2(L^3)_2(\mu-\text{CN})]\) where the shorter \(\text{CN}^-\) acts as a linear \(\mu_2-K\text{C}_{\text{ax}}\text{K}\) bridging donor. On the other hand, with \(L^3\) presenting two longer pendant arms as in \(L^3\), a linear \(\mu_2-K\text{C}_{\text{ax}}\text{K}\) bridging mode is observed in \([\text{Ag}_2(L^3)_2(\mu-\text{CN})]\) \(\text{BF}_4\) for the cyanide ligand, while a terminal coordination mode is observed for \(\text{NCS}^-\) in the mononuclear tetrahedral complex \([\text{Ag}(L^3)\text{(SCN)}]\). A side-on \(\mu_2-K\text{C}_{\text{ax}}\text{K}\) bridging mode is observed in \([\text{Ag}_2(L^3)_2(\mu-\text{CN})]\) \(\text{BF}_4\), where the macrocyclic ligand \(L^1\) incorporates shorter pendant arms compared to \(L^2\) and \(L^1\). 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 \(\text{CN}^-\) and \(\text{NCS}^-\).

Acknowledgements

We thank the University of Cagliari (Italy), the University of Nottingham (UK) and the EPSRC for support.

References


Figure 6
The asymmetric unit of complex \([\text{Ag}_2(L^3)_2(\mu-\text{SCN})]\) \(\text{BF}_4\), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
research papers


Coordination chemistry of nitrile-functionalized mixed thia-aza macrocycles [9]aneN₂S and [9]aneNS₂ towards silver(I)

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Computing details

Data collection: SMART (Bruker, 1998) for AgL₁₂BF₄, AgL₂SCN; STADI-4 (Stoe & Cie, 1996) for AgL₃₂μ-SCNB₄. Cell refinement: SMART (Bruker, 1998) for AgL₁₂BF₄, AgL₂SCN; STADI-4 (Stoe & Cie, 1996) for AgL₃₂μ-SCNB₄. Data reduction: SAINT (Bruker, 1999) for AgL₁₂BF₄, AgL₂SCN; X-RED (Stoe & Cie, 1996) for AgL₃₂μ-SCNB₄. 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-κ³N,N',S]silver(I) tetrafluoridoborate (AgL₁₂BF₄)

Crystal data

[Ag(C₁₀H₁₆N₄S)₂]BF₄

Z = 2
M_r = 643.33

Triclinic, P₁

a = 10.1813 (6) Å
b = 10.2237 (6) Å
c = 15.0154 (9) Å
α = 73.446 (2)°
β = 82.398 (2)°
γ = 61.781 (2)°
V = 1320.11 (14) Å³

Crystal data

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

Refinement

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.023

wR(F²) = 0.062

S = 1.07

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

\[ w = \frac{1}{\sigma^2(F_{o}^2) + (0.0381P)^2} \]
where \( P = (F_{o}^2 + 2F_{c}^2)/3 \)

\( (\Delta/\sigma)_{\text{max}} = 0.001 \)
\( \Delta \rho_{\text{max}} = 0.46 \text{ e Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.33 \text{ e Å}^{-3} \)

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 (Å²)

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<td>0.936645</td>
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<tr>
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<tr>
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Atomic displacement parameters (Å²)

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<th>U²³</th>
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<tr>
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<td>-0.0037 (6)</td>
<td>-0.0068 (6)</td>
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</table>

| Atomic displacement parameters (Å²) |

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<tr>
<th></th>
<th>U¹¹</th>
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<th>U¹³</th>
<th>U²²</th>
<th>U²³</th>
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<td>0.02112 (9)</td>
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<td>0.01874 (8)</td>
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<td>-0.0122 (7)</td>
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<td>0.0277 (8)</td>
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<td>-0.0163 (7)</td>
<td>-0.0037 (6)</td>
<td>-0.0068 (6)</td>
</tr>
</tbody>
</table>
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)  
C7′ | 0.0208 (7) | 0.0239 (7) | 0.0213 (6) | −0.0076 (6) | −0.0001 (5) | −0.0105 (5)  
N7′ | 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) | 0.0348 (9) | −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) | −0.0011 (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, °)**

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<th>Value</th>
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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 110.04 (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—C4 63.48 (17)  C3′—N4′—C5′—C6′ 58.55 (17)
C2—C3—N4—Ag1 −169.32 (14)  C3′—N4′—C5′—C6′ 58.55 (17)
C2—C3—N4—C41 −58.13 (14)  N4′—C5′—C6′—N7′ 98.00 (17)
C3—N4—C5—C6 60.17 (17)  N4′—C5′—C6′—N7′ 98.00 (17)
C3—N4—C5—C6 −136.60 (13)  N4′—C5′—C6′—N7′ 98.00 (17)
C3—N4—C41—C42 −62.98 (18)  N4′—C5′—C6′—N7′ 98.00 (17)
N4—C5—C6—N7 59.09 (17)  N4′—C5′—C6′—N7′ 98.00 (17)
N4—C5—C6—N7 −135.52 (14)  N4′—C5′—C6′—N7′ 98.00 (17)
C5—N4—C41—C42 65.45 (17)  N4′—C5′—C6′—N7′ 98.00 (17)
C5—C6—N7—C9 60.78 (17)  N4′—C5′—C6′—N7′ 98.00 (17)
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C6—N7—C9—C8 −134.70 (14)  N4′—C5′—C6′—N7′ 98.00 (17)
C6—N7—C9—C8 −63.56 (19)  N4′—C5′—C6′—N7′ 98.00 (17)
C8—S1—C2—C3 −116.31 (13)  N4′—C5′—C6′—N7′ 98.00 (17)
C9—N7—C71—C72 66.59 (17)  N4′—C5′—C6′—N7′ 98.00 (17)
C41—N4—C5—C6 95.72 (15)  N4′—C5′—C6′—N7′ 98.00 (17)
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-κ3N,N′,S](thiocyanato-κS)silver(I) (AgL2SCN)

Crystal data
[Ag(C12H20N4S)(NCS)]  Z = 2
Mr. = 418.33  F(000) = 424
Triclinic, P1  Dm = 1.661 Mg m−3
a = 8.4426 (6) Å  Mo Kα radiation, λ = 0.71073 Å
b = 8.5739 (6) Å  Cell parameters from 4102 reflections
 c = 11.8497 (8) Å  θ = 2.4–28.7°
α = 96.585 (1)°  μ = 1.46 mm−1
β = 99.023 (1)°  T = 150 K
γ = 95.313 (1)°  Block, colourless
V = 836.19 (1) Å³  0.36 × 0.30 × 0.07 mm
Data collection

Bruker SMART1000 CCD area-detector diffractometer
Graphite monochromator
Detector resolution: 8.336 pixels mm\(^{-1}\)
\(\omega\) scans
Absorption correction: integration
(SHELXTL; Sheldrick, 2008)
\(T_{\text{min}} = 0.606, T_{\text{max}} = 0.819\)

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
H-atom parameters constrained
\(w = 1/[\sigma(F_o^2) + (0.0321P)^2 + 0.1835P]\)
where \(P = (F_o^2 + 2F_c^2)/3\)

\(\Delta/\sigma)_{\text{max}} = 0.001\)
\(\Delta\rho_{\text{max}} = 0.34\ \text{e} \ \text{Å}^{-3}\)
\(\Delta\rho_{\text{min}} = -0.41\ \text{e} \ \text{Å}^{-3}\)

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\(^2\))

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### Atomic displacement parameters (Å²)

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### Geometric parameters (Å, °)

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C3—N4—C5 114.32 (14) N4—C41—C42 114.42 (15)
C5—N4—Ag1 102.34 (10) H41A—C41—H41B 107.6
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C41—N4—C5 112.35 (14) C42—C41—H41B 108.7
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C6—C5—H5B 108.8 C43—C42—H42B 109.5
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C5—N7—Ag1 111.38 (10) N7—C8—C9—S1 53.5 (2)
C8—N7—Ag1 113.24 (14) C6—N7—C8—C9 67.1 (2)
Ag1—S1—C2—C3 −52.45 (14) C6—N7—C8—C9 −162.91 (15)
Ag1—S1—C9—C8 −18.86 (15) C5—N7—C8—C9 177.8 (2)
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Ag1—N4—C41—C42 −170.34 (13) C5—C6—N7—Ag1 −58.6 (2)
Ag1—N7—C8—C9 −54.08 (16) C5—C6—N7—C8 −16.69 (18)
Ag1—N7—C71—C72 −168.44 (12) C5—C6—N7—C8 −133.28 (16)
S1—C2—C3—N4 −55.39 (19) C5—C6—N7—C8 97.45 (17)
C2—S1—C9—C8 −116.97 (15) C6—N7—C71—C72 −58.6 (2)
C2—C3—N4—Ag1 −23.22 (17) C71—N7—C72—C73 179.87 (15)
C2—C3—N4—Ag1 −138.19 (15) C8—N7—C71—C72 71.83 (19)
C2—C3—N4—Ag1 92.03 (18) C9—S1—C2—C3 50.32 (16)
C3—N4—C5—C6 61.40 (19) C9—S1—C2—C3 50.32 (16)
C3—N4—C41—C42 70.1 (2) C9—S1—C2—C3 50.32 (16)
N4—C5—C6—N7 54.1 (2)

µ-Thiocyanato-κ²S:S-bis([7-(2-cyanoethyl)-1,4-dithia-7-azacyclononane-κ³N,S,S′]silver(I)) tetrafluoridoborate
(Ag2L32mu-SCNBF4)

Crystal data

\[\text{[Ag}_2(C_9H_16N_2S_2)_2(SCN)]BF_4\]

\[\begin{align*}
    \text{Mr} &= 793.34 \\
    \text{Z} &= 8 \\
    a &= 28.537 (3) \text{ Å} \\
    b &= 8.4362 (11) \text{ Å} \\
    c &= 27.216 (3) \text{ Å} \\
    \beta &= 119.940 (9)^\circ
\end{align*}\]

\[V = 5677.6 (12) \text{ Å}^3\]

\[D_\lambda = 1.856 \text{ Mg m}^{-3}\]

\[\text{Mo K}\alpha \text{ radiation}, \lambda = 0.71073 \text{ Å}\]

Cell parameters from 35 reflections

\[\theta = 11.1\text{–}15.4^\circ\]

\[F(000) = 3168\]

\[D_\lambda = 1.856 \text{ Mg m}^{-3}\]
\( \mu = 1.79 \text{ mm}^{-1} \)
\( T = 150 \text{ K} \)
Tablet, colourless
0.27 \times 0.15 \times 0.12 \text{ mm}

Data collection
Stoe STADI4 4-circle diffractometer
Radiation source: fine-focus sealed tube
Planar graphite monochromator
Scan width (\( \omega \)) = 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)
\( T_{\text{min}} = 0.713, T_{\text{max}} = 0.822 \)
5547 measured reflections
4972 independent reflections
5547 reflections with \( I > 2\sigma(I) \)
\( R_{\text{int}} = 0.025 \)
\( \theta_{\text{max}} = 25.0^\circ, \theta_{\text{min}} = 2.6^\circ \)
\( h = -33 \rightarrow 33 \)
\( k = -10 \rightarrow 0 \)
\( l = -32 \rightarrow 32 \)
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 \( P = (F_o^2 + 2F_c^2)/3 \)
\( (\Delta/\sigma)_{\text{max}} = 0.001 \)
\( \Delta\rho_{\text{max}} = 0.56 \text{ e Å}^{-3} \)
\( \Delta\rho_{\text{min}} = -0.52 \text{ e Å}^{-3} \)
Extinction correction: SHELXL2018 (Sheldrick, 2015), \( F_c^* = kF_c[1+0.001xF_c^2/\lambda^2]^{-1/4} \)
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 (Å²)

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<th>y</th>
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*Acta Cryst. (2022), C78, 169-175* sup-16
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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)