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Crystal structure of $\text{Ag}_2(\mu\text{-SCN})_2(\text{NH}_3)_4$

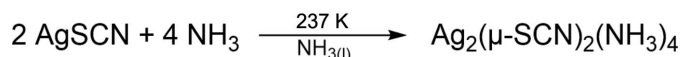
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Di- μ -thiocyanato-bis[diamminesilver(I)], $[\text{Ag}_2(\mu\text{-SCN})_2(\text{NH}_3)_4]$, was synthesized by the reaction of AgSCN with anhydrous liquid ammonia. In the binuclear molecule, the Ag^{I} atom is coordinated by two ammine ligands and the S atom of one thiocyanate ligand. Two of these $[\text{Ag}(\text{SCN})(\text{NH}_3)_2]$ units are bridged by the S atoms of the thiocyanate anions at longer distances, leading to a dimer with point group symmetry C_2 . The distance between the Ag^{I} atoms in the dimer is at 3.0927 (6) Å within the range of argentophilic interactions. The crystal structure displays $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen-bonding interactions that build up a three-dimensional network.

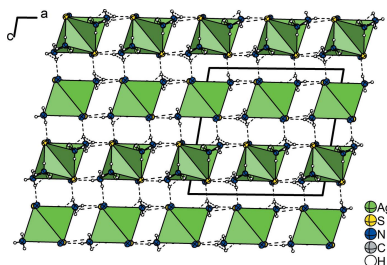
1. Chemical context

The reactions of various silver salts with liquid ammonia and their products are in almost all cases still unknown. In textbooks, the formation of the linear diamminesilver(I) cation is often predicted without any structural evidence. In this contribution we want to report on the reaction and the product of AgSCN with liquid ammonia at 237 K. A dinuclear Ag^{I} complex was obtained.



2. Structural commentary

All atoms are located on general sites. The silver atom Ag1 is surrounded by two ammine ligands (N2 and N3) with distances of 2.269 (2) and 2.248 (2) Å, respectively. These values are in good agreement with other reported Ag–N distances (Zachwieja & Jacobs, 1989). The thiocyanate anion coordinates with its soft sulfur atom to the silver atom at a distance of 2.5363 (6) Å, which is similar compared to those of pure AgSCN (Lindqvist, 1957). The S–C–N angle in this pseudo-halide anion is with 178.2 (2)° almost linear. Two of the $[\text{Ag}(\text{SCN})(\text{NH}_3)_2]$ units are connected to each other *via* bridging S atoms of the thiocyanato ligands into a dimer located about a twofold rotation axis (Fig. 1). The resulting coordination polyhedron around Ag1 is that of a distorted tetrahedron where one short Ag–S distance [2.5363 (6) Å] and a long one [3.0533 (7) Å] are observed. Therefore, the bond towards the latter may be regarded as weaker. In the dimer, the two tetrahedra are connected through one edge into a double tetrahedron. It is interesting to note that the two SCN^- anions point in the same direction as there is no center of inversion within the molecule but only the twofold rotation axis of the space-group type. The $\text{Ag}\cdots\text{Ag}$ distance is short at



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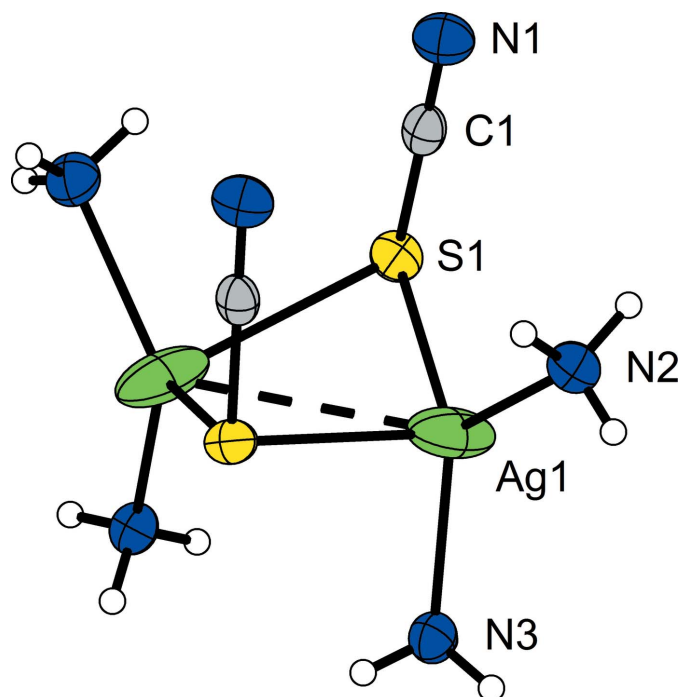


Figure 1
The dimeric $[\text{Ag}(\text{SCN})(\text{NH}_3)_2]_2$ unit in the title compound. Displacement ellipsoids are shown at the 70% probability level and H atoms are drawn with an arbitrary radius. All non-labelled atoms are generated by symmetry code $(-x, y, -z + \frac{1}{2})$.

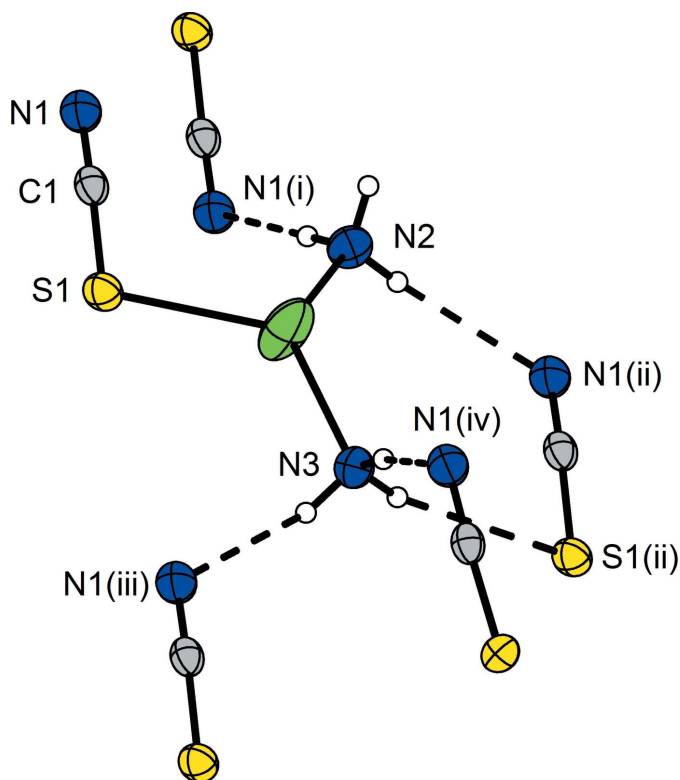


Figure 2
The hydrogen bonds (dashed lines) present in the structure of the title compound as illustrated for one $[\text{Ag}(\text{SCN})(\text{NH}_3)_2]$ unit with the acceptor groups of four surrounding molecules. Displacement ellipsoids as in Fig. 1. [Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $x, y - 1, z$; (iv) $-x, y - 1, -z + \frac{1}{2}$.]

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N2}-\text{H2C} \cdots \text{N1}^{\text{i}}$	0.89 (4)	2.34 (4)	3.230 (3)	171 (3)
$\text{N2}-\text{H2B} \cdots \text{N1}^{\text{ii}}$	0.83 (5)	2.43 (5)	3.255 (3)	170 (4)
$\text{N3}-\text{H3C} \cdots \text{N1}^{\text{iii}}$	0.90 (4)	2.31 (4)	3.128 (3)	151 (3)
$\text{N3}-\text{H3B} \cdots \text{N1}^{\text{iv}}$	0.83 (4)	2.39 (4)	3.208 (3)	168 (4)
$\text{N3}-\text{H3A} \cdots \text{S1}^{\text{ii}}$	0.87 (4)	2.82 (4)	3.672 (2)	166 (3)

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

3.0927 (6) \AA , and is clearly in the range of argentophilic interactions (Jansen, 1987; Zachwieja & Jacobs, 1989; Schmidbauer & Schier, 2015).

3. Supramolecular features

The dinuclear complexes are connected to others *via* hydrogen bonds between the ammine ligands (N2 and N3) as donors and the N1 and S1 atoms of the thiocyanato ligand as acceptors. A three-dimensional network is formed in which each $[\text{Ag}(\text{SCN})(\text{NH}_3)_2]$ unit is coordinated by four (Fig. 2) and the dimer by eight other molecules. Six are arranged like a hexagon around the central molecule with all SCN ligands pointing in the same direction. Two molecules reside above and below this fictitious plane and are shifted towards a corner of the hexagon whereby the SCN ligands point in the opposite direction. Each of these two molecules shows the same coordination as described above, and overall, an *AB*-stacking of the molecules along $[001]$, similar to the hexagonal closest packing, is obtained. The crystal structure is shown in Fig. 3. It should be noted that no acceptor atom for the hydrogen atom H2A is present in the neighbourhood within the range of the sum of the van der Waals radii of H and N atoms. Numerical details of the hydrogen bonding are given in Table 1.

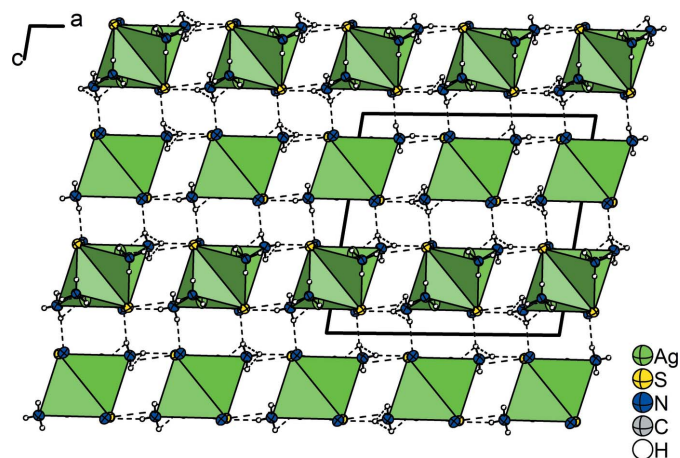


Figure 3
The crystal structure of $\text{Ag}_2(\text{SCN})_2(\text{NH}_3)_4$ viewed along $[010]$ with hydrogen bonds (dashed lines). Displacement ellipsoids as in Fig. 1.

Table 2

Experimental details.

Crystal data	
Chemical formula	[Ag ₂ (SCN) ₂ (NH ₃) ₄]
<i>M_r</i>	400.04
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.8263 (9), 7.1879 (3), 12.2478 (9)
β (°)	98.936 (6)
<i>V</i> (Å ³)	1115.47 (12)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.85
Crystal size (mm)	0.26 × 0.16 × 0.14
Data collection	
Diffractometer	Stoe <i>IPDS</i> 2T
Absorption correction	Numerical (<i>X-RED32</i> and <i>X-SHAPE</i> ; Stoe & Cie, 2009)
<i>T</i> _{min} , <i>T</i> _{max}	0.768, 0.918
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	7257, 1690, 1593
<i>R</i> _{int}	0.028
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.714
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.029, 0.061, 1.11
No. of reflections	1690
No. of parameters	79
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.26, -1.82

Computer programs: *X-AREA* (Stoe & Cie, 2001), *X-RED32* (Stoe & Cie, 2009), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *SHELXL* (Hübschle *et al.*, 2011), *DIAMOND* (Brandenburg, 2015) and *pubCIF* (Westrip, 2010).

4. Synthesis and crystallization

400 mg (2.41 mmol) of AgSCN were placed in a flame-dried Schlenk tube under argon. Approximately 0.5 ml of liquid

ammonia were condensed into the reaction vessel. The reaction vessel was stored at 237 K. After two weeks, colorless crystals of suitable size for X-ray diffraction were obtained from the colorless solution. The formation of the title compound is shown in the scheme.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms of the ammine ligands were located from a difference Fourier map and were refined isotropically without further restraints.

Acknowledgements

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Crystal structure of $\text{Ag}_2(\mu\text{-SCN})_2(\text{NH}_3)_4$

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2011); cell refinement: *X-AREA* (Stoe & Cie, 2011); data reduction: *X-RED32* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b) and *SHELXLE* (Hübschle *et al.*, 2011); molecular graphics: *DIAMOND* (Brandenburg, 2015); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

Di- μ -thiocyanato-bis[diamminesilver(I)]

Crystal data

$[\text{Ag}_2(\text{SCN})_2(\text{NH}_3)_4]$

$M_r = 400.04$

Monoclinic, *C2/c*

$a = 12.8263$ (9) Å

$b = 7.1879$ (3) Å

$c = 12.2478$ (9) Å

$\beta = 98.936$ (6)°

$V = 1115.47$ (12) Å³

$Z = 4$

$F(000) = 768$

$D_x = 2.382$ Mg m⁻³

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

Cell parameters from 13119 reflections

$\theta = 3.2\text{--}35.2^\circ$

$\mu = 3.85$ mm⁻¹

$T = 100$ K

Block, colorless

$0.26 \times 0.16 \times 0.14$ mm

Data collection

Stoe IPDS 2T

diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm⁻¹

rotation method scans

Absorption correction: numerical

(*X-RED32* and *X-SHAPE*; Stoe & Cie, 2009)

$T_{\min} = 0.768$, $T_{\max} = 0.918$

7257 measured reflections

1690 independent reflections

1593 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 30.5^\circ$, $\theta_{\min} = 3.2^\circ$

$h = -18 \rightarrow 18$

$k = -10 \rightarrow 9$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.061$

$S = 1.11$

1690 reflections

79 parameters

0 restraints

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0131P)^2 + 6.0057P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 1.26$ e Å⁻³

$\Delta\rho_{\min} = -1.82$ e Å⁻³

Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ag1	0.06012 (2)	0.01303 (3)	0.14990 (3)	0.04102 (10)
S1	-0.13234 (4)	0.10809 (8)	0.10715 (5)	0.01844 (11)
N1	-0.11243 (17)	0.4982 (3)	0.10139 (18)	0.0226 (4)
N2	0.17384 (18)	0.2371 (3)	0.11205 (19)	0.0217 (4)
N3	0.10144 (16)	-0.2907 (3)	0.16630 (18)	0.0189 (4)
C1	-0.11906 (16)	0.3371 (3)	0.10457 (17)	0.0162 (4)
H2A	0.187 (3)	0.315 (6)	0.169 (3)	0.037 (10)*
H2B	0.228 (3)	0.181 (7)	0.101 (4)	0.050 (12)*
H2C	0.150 (3)	0.311 (5)	0.055 (3)	0.034 (9)*
H3A	0.158 (3)	-0.322 (5)	0.140 (3)	0.029 (9)*
H3B	0.110 (3)	-0.331 (5)	0.231 (3)	0.033 (9)*
H3C	0.050 (3)	-0.355 (6)	0.125 (3)	0.039 (10)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.02898 (12)	0.02005 (11)	0.0765 (2)	0.00256 (8)	0.01589 (11)	0.01630 (11)
S1	0.0185 (2)	0.0165 (2)	0.0201 (2)	-0.00265 (19)	0.00216 (18)	0.00010 (19)
N1	0.0216 (9)	0.0201 (10)	0.0247 (10)	0.0003 (7)	-0.0008 (7)	-0.0002 (8)
N2	0.0245 (10)	0.0190 (9)	0.0220 (10)	0.0006 (8)	0.0048 (8)	0.0022 (8)
N3	0.0177 (9)	0.0204 (9)	0.0191 (9)	0.0000 (7)	0.0045 (7)	0.0008 (7)
C1	0.0139 (9)	0.0217 (10)	0.0126 (8)	0.0000 (7)	0.0009 (7)	-0.0011 (8)

Geometric parameters (\AA , $^\circ$)

Ag1—N3	2.248 (2)	N2—H2A	0.89 (4)
Ag1—N2	2.269 (2)	N2—H2B	0.83 (5)
Ag1—S1	2.5363 (6)	N2—H2C	0.89 (4)
Ag1—S1 ⁱ	3.0533 (7)	N3—H3A	0.87 (4)
Ag1—Ag1 ⁱ	3.0927 (6)	N3—H3B	0.83 (4)
S1—C1	1.656 (2)	N3—H3C	0.90 (4)
N1—C1	1.162 (3)		
N3—Ag1—N2	123.89 (8)	Ag1—N2—H2C	115 (2)
N3—Ag1—S1	119.24 (6)	H2A—N2—H2C	104 (3)
N2—Ag1—S1	113.74 (6)	H2B—N2—H2C	111 (4)
N3—Ag1—Ag1 ⁱ	93.95 (5)	Ag1—N3—H3A	115 (2)
N2—Ag1—Ag1 ⁱ	125.28 (6)	Ag1—N3—H3B	115 (3)
S1—Ag1—Ag1 ⁱ	64.820 (16)	H3A—N3—H3B	105 (3)

C1—S1—Ag1	99.91 (8)	Ag1—N3—H3C	108 (3)
Ag1—N2—H2A	109 (3)	H3A—N3—H3C	104 (3)
Ag1—N2—H2B	105 (3)	H3B—N3—H3C	109 (3)
H2A—N2—H2B	113 (4)	N1—C1—S1	178.2 (2)

Symmetry code: (i) $-x, y, -z+1/2$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N2—H2C...N1 ⁱⁱ	0.89 (4)	2.34 (4)	3.230 (3)	171 (3)
N2—H2B...N1 ⁱⁱⁱ	0.83 (5)	2.43 (5)	3.255 (3)	170 (4)
N3—H3C...N1 ^{iv}	0.90 (4)	2.31 (4)	3.128 (3)	151 (3)
N3—H3B...N1 ^v	0.83 (4)	2.39 (4)	3.208 (3)	168 (4)
N3—H3A...S1 ⁱⁱⁱ	0.87 (4)	2.82 (4)	3.672 (2)	166 (3)

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