Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# *catena*-Poly[1,4-diazoniabicyclo-[2.2.2]octane [silver(I)-tri-$\mu$-thiocyanato-$\kappa^6S$:$S$]]

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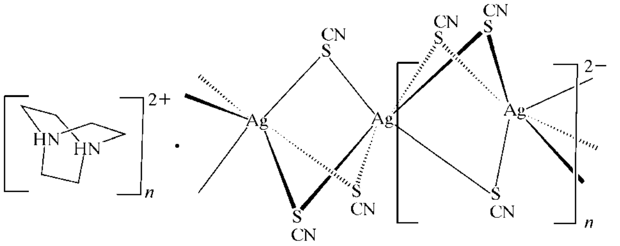
Received 22 June 2004
Accepted 19 July 2004
Online 11 August 2004

The title compound, $\{(C_6H_{14}N_2)[Ag(NCS)_3]\}_n$, is a polymeric silver(I) complex. The Ag$^I$ atom is hexacoordinated by the S atoms of six thiocyanate anions, with each thiocyanate S atom acting in a bridging mode to link the Ag atoms together. The unique Ag$^I$ atom lies at a cell origin and has crystallographically imposed $\overline{3}$ symmetry. The diazonia[2.2.2]octane molecule lies about a site with $\overline{6}$ imposed symmetry with the unique N atom on a threefold axis. The S and N atoms of the thiocyanate ligands sit on a mirror plane and a threefold axis, respectively. The crystal structure consists of one-dimensional chains, which are stabilized by N—H···N hydrogen bonds to form a three-dimensional network.

## Comment

The silver(I) cation is good candidate as a soft acid, favouring coordination to soft bases, such as ligands containing S and N atoms. Because of this, we and others have exploited the coordination flexibility of silver(I) in the construction of a large number of coordination polymers, which exhibit interesting structural diversity (Yang *et al.*, 2000; Zhu, Zhang *et al.*, 2003; Zhu *et al.*, 2004). Thiocyanate is a potential bridging ligand. Thus, many complexes containing AgSCN units have been reported (Cotton & Wilkinson, 1988; Krautscheid *et al.*, 1998; Ren *et al.*, 2001). In this paper, we report the title novel silver(I) thiocyanate salt, (I).



(I)

Compound (I) is a polymeric silver(I) complex. The unique Ag$^I$ atom lies at a cell origin and has crystallographically imposed $\overline{3}$ symmetry. The S and N atoms of the thiocyanate ligands sit on the mirror plane and threefold axis, respectively, with site-occupancy factors of $\frac{1}{2}$ and $\frac{1}{3}$, respectively.

The Ag atom is pseudo-octahedrally six-coordinated by three pairs of bridging S atoms, which link the Ag atoms together to form a one-dimensional polymeric chain (Fig. 1). The smallest repeat unit consists of a silver–thiocyanate–1,4-diazoniabicyclo[2.2.2]octane adduct in a 1:3:1 stoichiometry, in which 1,4-diazoniabicyclo[2.2.2]octane acts as a cation, not as a coordination ligand to the Ag atom. The six Ag—S bonds are the same [2.7993 (15) Å] and are normal by comparison with those in a similar complex (Zhu, Liu & Meng, 2003). The bond angles are in the range 83.35 (4)–96.65 (4)° at the Ag atom, so each Ag atom lies almost at the centre of a slightly distorted octahedron. The thiocyanate group is almost linear [S—C = 1.645 (8) Å, and C—N = 1.490 (5) Å, and S—C—N = 179.5 (7)°]. The Ag—S—Ag angle is 79.69 (5)°. The remaining

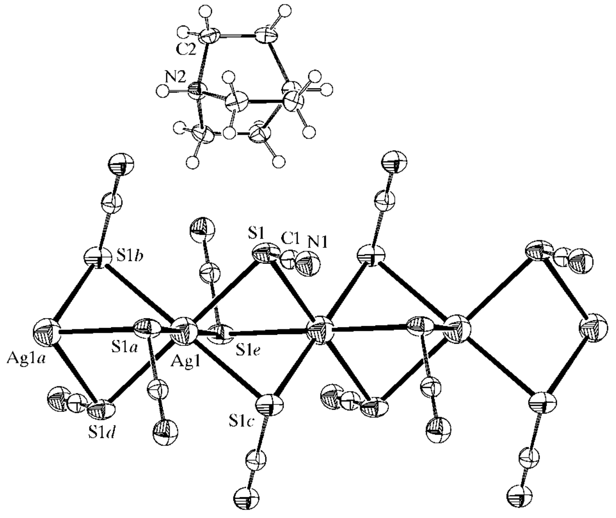


**Figure 1**
A view of (I) along the *a* axis. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (*a*) $1+x-y$, $x$, $-\frac{1}{2}+z$; (*b*) $y$, $1-x+y$, $-\frac{1}{2}+z$; (*c*) $2-y$, $1+x-y$, $z$; (*d*) $2-x$, $2-y$, $-\frac{1}{2}+z$; (*e*) $1-x+y$, $2-x$, $z$.]

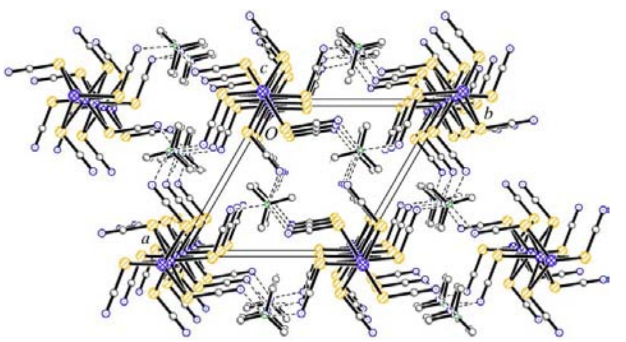


**Figure 2**
The crystal packing of (I), showing the N—H···N hydrogen-bonding interactions as dashed lines. H atoms not involved in the hydrogen bonds have been omitted for clarity.

DOI: 10.1107/S010827010401772X

C—S—Ag angles about the S atom are both 106.89 (19)°, so that the geometry at the S atom is a slightly distorted pyramid.

In the crystal structure of (I), the bridging S atoms link the Ag atoms into a linear chain along the *c* axis. The diazonia[2.2.2]octane cations lie about sites with $\overline{6}$ symmetry and are located between the chains. Adjacent chains interact with the cations *via* three equivalent hydrogen bonds [N2—H3$\cdots$N1$^{i}$/N1$^{ii}$/N1$^{iii}$; symmetry codes: (i) $1 - x$, $1 - y$, $-z$; (ii) $x - y$, $x$, $-z$; (iii) $y$, $1 - x + y$, $-z$], forming a three-dimensional structure (Fig. 2).

## Experimental

$AgNO_3$ (0.170 g, 1 mmol) and 1,4-diazabicyclo[2.2.2]octane (0.5 ml) were dissolved in ammonia solution (10 ml, 30%) and the mixture was stirred for about 30 min at room temperature. The resulting clear colourless solution was allowed to stand in air and, after slow evaporation of the solvent over a period of 15 d, large colourless crystals of (I) formed at the bottom of the vessel. The crystals were isolated, washed three times with water and dried in a vacuum desiccator using $CaCl_2$ (yield 52.8%). Analysis found: C 27.32, H 3.48, N 17.62, S 24.31%; calculated for $C_9H_{14}AgN_5S_3$: C 27.28, H 3.56, N 17.67, S 24.27%.

### *Crystal data*

$(C_6H_{14}N_2)[Ag(NCS)_3]$
$M_r$ = 396.30
Hexagonal, $P6_3/m$
$a$ = 10.2148 (14) Å
$c$ = 7.1740 (14) Å
$V$ = 648.26 (18) Å$^3$
$Z$ = 2
$D_x$ = 2.030 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 506 reflections
$\theta$ = 3–28°
$\mu$ = 2.03 mm$^{-1}$
$T$ = 293 (2) K
Needle, colourless
0.30 × 0.10 × 0.08 mm

### *Data collection*

Siemens SMART CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.582, $T_{max}$ = 0.855
3024 measured reflections
506 independent reflections
489 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.160
$\theta_{max}$ = 27.0°
$h = -13 \rightarrow 8$
$k = -12 \rightarrow 13$
$l = -9 \rightarrow 8$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.168
$S$ = 1.06
506 reflections
43 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 3.05P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.81 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.69 e Å$^{-3}$

**Table 1**
Hydrogen-bonding geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N2—H3$\cdots$N1$^{i}$ | 0.91 (2) | 2.443 (14) | 3.070 (7) | 125.9 (4) |

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

All H atoms were located in difference Fourier maps and refined isotropically [C—H = 0.86 (5) and 0.86 (6) Å; see Table 1 for N—H distance].

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

The authors thank the Education Office of Anhui Province, People's Republic of China, for research grant No. 2004kj300zd.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1193). Services for accessing these data are described at the back of the journal.

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