

**$\gamma$ -Modification of poly[(*N,N*-diethyl-dithiocarbamato)silver(I)]**

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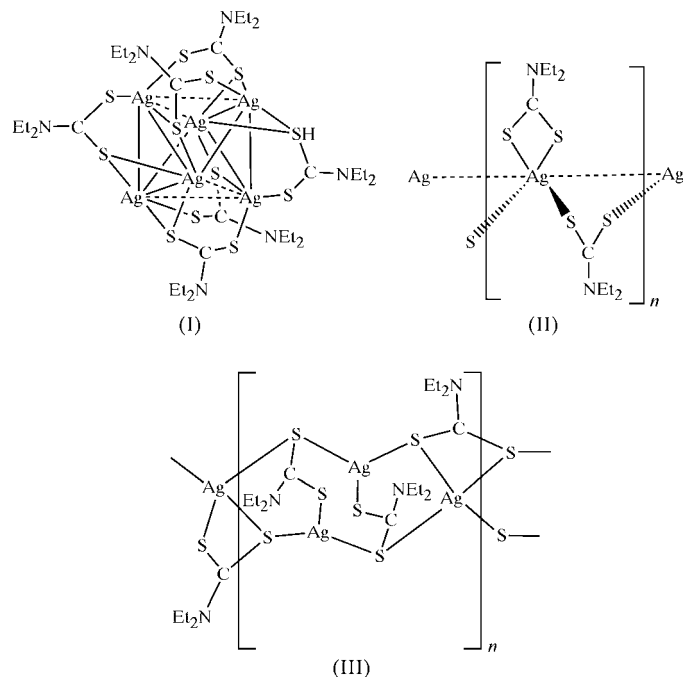
In the title compound, *catena*-poly[[trisilver(I)-tri- $\mu_3$ -*N,N*-diethyldithiocarbamato-3' $\kappa$ S:1 $\kappa$ S':2 $\kappa$ S;1 $\kappa$ S:2 $\kappa$ S':3 $\kappa$ S;2 $\kappa$ S:3 $\kappa^2$ -S,S':1' $\kappa$ S'], [Ag<sub>3</sub>(C<sub>5</sub>H<sub>10</sub>NS<sub>2</sub>)<sub>3</sub>]<sub>n</sub>, the trigonally and tetrahedrally coordinated Ag atoms are  $\mu_3$ -bridged by  $\kappa^3$ - and  $\kappa^4$ -S<sub>2</sub>CNEt<sub>2</sub> ligands to form a ribbon structure along the *c* axis. There is a twofold axis parallel to the *b* axis and passing through the tetrahedrally coordinated Ag atom. The S<sub>2</sub>CNEt<sub>2</sub> ligands coordinate the Ag atoms in  $\eta^1, \eta^2$ - and  $\eta^2, \eta^2$ -fashions, depending on the bridging S atoms. The distances between the trigonal Ag and S atoms are 2.4915 (11)–2.6205 (11) Å, while those between the tetrahedral Ag and S atoms are 2.5457 (11) and 2.7145 (10) Å. The shortest Ag...Ag distance between trigonal Ag atoms is 2.8336 (7) Å, which indicates a weak Ag...Ag interaction, whereas the shortest distance between trigonal and tetrahedral Ag atoms is 3.463 (6) Å, which is considered as non-bonding.

**Comment**

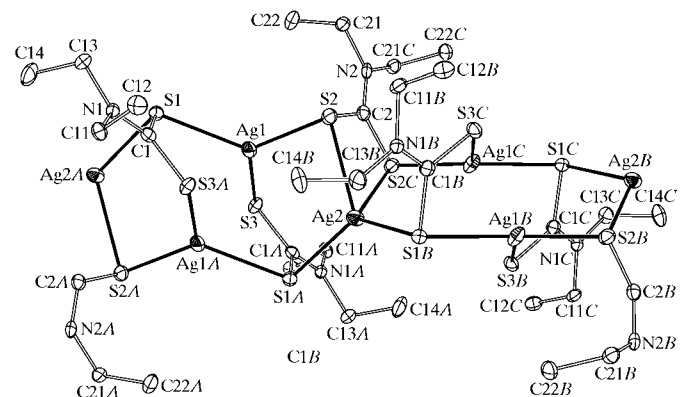
Dithiocarbamates (R<sub>2</sub>NCS<sub>2</sub><sup>-</sup>) are a versatile class of mono-anionic 1,1'-dithio ligand and, as they are easily prepared, a wide range of chemistry has been developed around them (Cocouvanis, 1979). The chemistry of transition metal-dithiocarbamate complexes is still of much current interest because of their applications in inorganic analysis, such as the separation of different metal ions by high-performance liquid chromatography (Liška *et al.*, 1979) and capillary gas chromatography (Riekkola, 1982), and as rubber vulcanization accelerators, fungicides and pesticides (Hogarth, 2005). A large number of transition metal-dithiocarbamate complexes have been synthesized to date and these have been reported to exhibit very abundant reactivities and a variety of structures (Hogarth, 2005).

Simple silver(I)-dithiocarbamate complexes, [Ag(S<sub>2</sub>CN-R<sub>2</sub>)<sub>n</sub>], have been known since the 1950s (Akerström, 1959), yet in the intervening years little work had been carried out. The low solubility of these complexes has probably hindered research in this field. Early crystallographic studies revealed the hexameric nature of Ag-S<sub>2</sub>CNR<sub>2</sub> (R = Et and Pr)

complexes in the solid state (Hesse, 1963), although in solution they are believed to be in equilibrium with the monomeric species. Recently, the silver-*N,N*-diethyldithiocarbamate complex has been the subject of two further crystallographic studies. The known monoclinic  $\alpha$ -modification, (I), characterized by X-ray powder diffraction data, is hexameric and consists of a distorted octahedron of Ag atoms (Hesse & Nilson, 1969). The dithiocarbamate anions cap six of the faces in a  $\eta^1, \eta^2$ -fashion; the remaining two faces, with long silver-silver interactions, remain uncapped. The  $\beta$ -modification, (II),



characterized by single-crystal X-ray diffraction, exhibits a polymeric chain structure in which each Ag atom is coordinated in a distorted fashion by three dithiocarbamate ligands (Anacker-Eickhoff *et al.*, 1982), one acting as a chelate and the others acting as  $\mu_2$ -bridges. Although the reaction of the

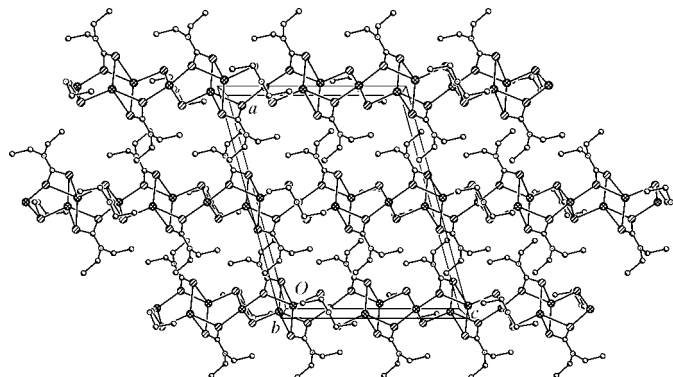


**Figure 1**  
 A view of the structure of (III), showing atomic displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (A) 1 - *x*, 1 - *y*, 1 - *z*; (B) *x*, 1 - *y*, ½ + *z*; (C) 1 - *x*, *y*, ½ - *z*.]

hexameric  $\alpha$ -modification,  $[\text{Ag}(\text{S}_2\text{CNET}_2)]_6$ , with  $(\text{SCN})_2$  resulted in the formation of the postulated products  $[\text{Ag}_6(\text{S}_2\text{CNET}_2)_5(\text{SCN})]$  and  $[\text{Ag}_6(\text{S}_2\text{CNET}_2)_6(\text{SCN})_4]$  (Calabro *et al.*, 1981), poor solubility in common organic solvents made characterization of the complexes possible only on the basis of spectroscopic data; accordingly, no X-ray crystallographic study was reported. Huang *et al.* (1992) prepared a polynuclear silver(I)-diethyldithiocarbamate cluster,  $[\text{Ag}_{11}\text{S}(\text{S}_2\text{CNET}_2)_9]$ , with a centered  $\mu_5$ -S atom. One of us also isolated and crystallographically characterized an Se analog,  $[\text{Ag}_{11}(\mu_5\text{-Se})(\mu_3\text{-S}_2\text{CNET}_2)_6(\mu_4\text{-S}_2\text{CNET}_2)_3]$ , which contains six triply and three quadruply bridging dithiocarbamate ligands (Zhang *et al.*, 1998). We have maintained an interest in silver(I)-dithiocarbamate complexes and we report here the structure of the title compound, (III), which is the  $\gamma$ -modification of  $[\text{Ag}(\text{S}_2\text{CNET}_2)]_n$ .

Compound (III) has a polymeric structure (Fig. 1). There is a twofold axis through atoms Ag2, C2 and N2. The trigonally and tetrahedrally coordinated Ag atoms are  $\mu_3$ -bridged by  $\kappa^3$ - and  $\kappa^4$ - $\text{S}_2\text{CNET}_2$  ligands to form a ribbon structure along the *c* axis (Fig. 2). Similar to (I) (Hesse & Nilson, 1969) and (II) (Anacker-Eickhoff *et al.*, 1982), the formula of (III) is also defined as  $[\text{Ag}(\text{S}_2\text{CNET}_2)]_n$  on the basis of X-ray analysis, together with microanalyses and spectroscopy. We conclude that it is reasonable to name complex (III), which has a new structural mode, as the  $\gamma$ -modification of  $[\text{Ag}(\text{S}_2\text{CNET}_2)]_n$ . The  $\text{S}_2\text{CNET}_2$  ligands coordinate the Ag atoms in  $\eta^1, \eta^2$ - and  $\eta^2, \eta^2$ -fashions, depending on the bridging S atoms.

The distances between the trigonal Ag (Ag1) and S atoms are in the range 2.4915 (11)–2.6205 (11) Å (Table 1), and the S–Ag1–S bond angles are in the range 109.49 (4)–128.56 (3)°, indicating a highly distorted coordination geometry around atom Ag1. The tetrahedral Ag atom (Ag2) is bound by two  $\mu_2$ -S atoms from two  $\eta^1, \eta^2$ - $\text{S}_2\text{CNET}_2$  ligands and chelated by two  $\mu_2$ -S atoms from one  $\eta^2, \eta^2$ - $\text{S}_2\text{CNET}_2$  ligand. The coordination geometry of atom Ag2 is severely distorted, as observed in other silver–dithiocarbamate complexes with tetrahedral Ag atoms, such as  $[\text{Ag}(\text{S}_2\text{CNC}_4\text{H}_9)(\text{PPh}_3)_2]$  (Othman *et al.*, 1996) and  $[\text{Ag}(\text{S}_2\text{CNET}_2)(\text{PF}_6\text{Ph})]$  (Fc is ferrocenyl; Gimeno *et al.*, 1998). The distortion arises from the restricted bite angle S2–Ag2–S2C [67.15 (4)°; symmetry



**Figure 2**  
The crystal structure of (III), projected along the *b* axis. H atoms have been omitted for clarity.

codes *A–C* are as in Fig. 1]. There is also a large deviation of the S1A–Ag2–S1B angle [125.84 (4)°] from the ideal tetrahedral value. Each tetrahedral Ag atom has a pair of long and short Ag–S bonds [Ag2–S2 = 2.7145 (10) Å and Ag2–S1A = 2.5457 (11) Å]; interatomic Ag··S distances longer than 2.80 Å are considered to be non-bonding. The Ag··Ag distance between two adjacent trigonal Ag atoms [2.8336 (7) Å] is shorter than twice the van der Waals radius (1.7 Å) of Ag atoms, indicating a weak Ag··Ag interaction, which is obviously compatible with the Ag··Ag distance for metallic Ag atoms [2.889 (6) Å]. The reported Ag··Ag distances where bonding is considered to occur are in the range 2.729–3.065 Å (Kanatidis & Huang, 1989; Huang *et al.*, 1992; Yam *et al.*, 1996; Zhang *et al.*, 1998). The separation of adjacent trigonal and tetrahedral Ag atoms is 3.463 (6) Å, indicating that these atoms are non-bonded. The C–S bond lengths [1.714 (4)–1.751 (3) Å] are comparable to those in related silver–dithiocarbamate complexes. The C1–N1 and C2–N2 bond lengths are 1.325 (4) and 1.322 (6) Å, respectively, suggesting considerable partial double-bond character because the N-atom lone pair is involved in delocalized  $\pi$ -bonding over the NCS<sub>2</sub> group (Eisenberg, 1970).

## Experimental

Compound (III) was prepared by mixing stoichiometric quantities of  $\text{NaS}_2\text{CNET}_2 \cdot 3\text{H}_2\text{O}$  (225 mg, 0.10 mmol) and  $\text{Ag}(\text{CF}_3\text{SO}_3)$  (257 mg, 0.10 mmol) in absolute ethanol. The mixture was stirred for 15 min at room temperature. The resulting brown precipitate was filtered off and further recrystallized from dimethylformamide/tetrahydrofuran (1:5 *v/v*). Dark-red crystals of (III) were obtained after a few weeks (yield 116 mg, 45%). <sup>1</sup>H NMR (DMSO-*d*<sup>6</sup>):  $\delta$  1.23 (*m*, CH<sub>3</sub>), 3.54 (*m*, CH<sub>2</sub>). MS (FAB): *m/z* 256 (*M*<sup>+</sup> + 1). IR (KBr pellet, cm<sup>-1</sup>):  $\nu(\text{C}=\text{N})$  1479 (*s*);  $\nu(\text{C}=\text{S})$  990 (*s*), 917 (*m*). Analysis calculated for C<sub>9</sub>H<sub>30</sub>Ag<sub>3</sub>N<sub>3</sub>S<sub>6</sub>: C 23.35, H 3.94, N 5.47%; found: C 23.25, H 3.91, N 5.43%.

### Crystal data

$[\text{Ag}_3(\text{C}_5\text{H}_{10}\text{NS}_2)_3]$   
*M<sub>r</sub>* = 768.45  
Monoclinic, *C*2/*c*  
*a* = 18.138 (4) Å  
*b* = 9.5890 (19) Å  
*c* = 14.245 (3) Å  
 $\beta$  = 105.30 (3)°  
*V* = 2389.8 (8) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 2.136 Mg m<sup>-3</sup>  
Mo *K* $\alpha$  radiation  
Cell parameters from 2887 reflections  
 $\theta$  = 2.3–18.3°  
 $\mu$  = 2.97 mm<sup>-1</sup>  
*T* = 153 (2) K  
Prism, dark red  
0.25 × 0.22 × 0.18 mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.457, *T<sub>max</sub>* = 0.586  
7241 measured reflections

2853 independent reflections  
2506 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.031  
 $\theta_{\text{max}}$  = 28.3°  
*h* = –24 → 23  
*k* = –12 → 12  
*l* = –11 → 18

### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.079$   
*S* = 1.09  
2853 reflections  
124 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 2.307P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 1.59 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.97 \text{ e } \text{Å}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Ag1–S2	2.4915 (11)	Ag1–S3 <sup>i</sup>	2.9308 (10)
Ag1–S3	2.5333 (11)	Ag2–S1 <sup>i</sup>	2.5457 (11)
Ag1–S1	2.6205 (11)	Ag2–S2	2.7145 (10)
Ag1–Ag1 <sup>i</sup>	2.8336 (7)		
S2–Ag1–S3	119.54 (4)	S1–Ag1–S3 <sup>i</sup>	65.19 (3)
S2–Ag1–S1	128.56 (3)	S1 <sup>ii</sup> –Ag2–S1 <sup>i</sup>	125.84 (4)
S3–Ag1–S1	109.49 (4)	S1 <sup>iii</sup> –Ag2–S2	107.63 (3)
S2–Ag1–S3 <sup>i</sup>	101.75 (3)	S1 <sup>i</sup> –Ag2–S2	117.10 (3)
S3–Ag1–S3 <sup>i</sup>	118.03 (2)	S2 <sup>iii</sup> –Ag2–S2	67.15 (4)

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

All H atoms were found in difference density maps but were then placed in calculated positions ( $C-H = 0.96-0.97$  Å) and included in the refinement using a riding-model approximation, with  $U_{iso}(H)$  values of 1.2 or 1.5 times  $U_{eq}(C)$ . The largest peak in the final difference map is in the vicinity of the Ag atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB3001). Services for accessing these data are described at the back of the journal.

## References

- Akerström, S. (1959). *Ark. Kemi*, **14**, 413–420.
- Anacker-Eickhoff, H., Hesse, R., Jenische, P. & Wahlberg, A. (1982). *Acta Chem. Scand. Ser. A*, **81**, 255–264.
- Bruker (1998). *SMART* and *SAINT-Plus*. Versions 6.02a. Bruker AXS Inc., Madison, Wisconsin, USA.
- Calabro, D. C., Harrison, B. A., Palmer, G. T., Moguel, M. K. & Burmeister, J. L. (1981). *Inorg. Chem.* **20**, 4311–4316.
- Coucouvanis, D. (1979). *Prog. Inorg. Chem.* **26**, 301–387.
- Eisenberg, R. (1970). *Prog. Inorg. Chem.* **12**, 295–342.
- Gimeno, M. C., Jones, P. C., Laguna, A. & Sarroca, C. (1998). *Polyhedron*, **17**, 3681–3688.
- Hesse, R. (1963). *Ark. Kemi*, **20**, 481–486.
- Hesse, R. & Nilson, L. (1969). *Acta Chem. Scand.* **23**, 825–833.
- Hogarth, G. (2005). *Prog. Inorg. Chem.* **53**, 71–561.
- Huang, Z., Lei, X., Hong, M. & Liu, H. (1992). *Inorg. Chem.* **31**, 2990–2991.
- Kanatzidis, M. G. & Huang, S.-P. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1513–1515.
- Liška, O., Guichon, G. & Colin, H. (1979). *J. Chromatogr.* **171**, 145–152.
- Othman, A. H., Fun, H.-K. & Sivakumar, K. (1996). *Acta Cryst. C* **52**, 843–845.
- Riekkola, M. L. (1982). *Mikrochim. Acta*, **1**, 327–334.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997a). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Yam, V. W. W., Lo, K. K. W., Wang, C. R. & Cheung, K. K. (1996). *Inorg. Chem.* **35**, 5116–5120.
- Zhang, Q. F., Cao, R., Hong, M. C., Su, W. P. & Liu, H. Q. (1998). *Inorg. Chim. Acta*, **277**, 171–175.