

# Poly[( $\mu_3$ -*N,N*-dibenzylidithiocarbamato- $\kappa^4$ S,S':S:S')silver(I)]

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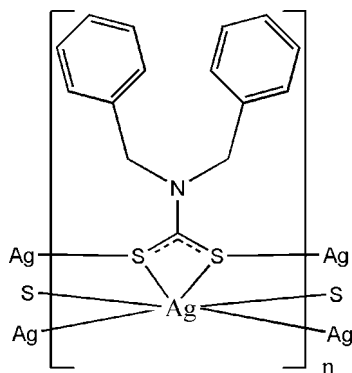
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.014$  Å;  $R$  factor = 0.045;  $wR$  factor = 0.080; data-to-parameter ratio = 14.5.

The title  $\text{Ag}^{\text{I}}$  coordination polymer,  $[\text{Ag}(\text{C}_{15}\text{H}_{14}\text{NS}_2)]_n$ , was synthesized by a solvothermal reaction of  $\text{AgNO}_3$  with sodium *N,N*-dibenzylidithiocarbamate in a methanol solution. The compound displays a helical structure and each  $\text{Ag}^{\text{I}}$  ion is four-coordinated by four S atoms from two dithiocarbamate ligands and can be described as a distorted tetrahedral configuration. While the  $\text{Ag}^{\text{I}}$  ions are bridged by both S atoms of the dithiocarbamate group to form the polymeric structure, the  $\text{Ag}\cdots\text{Ag}$  distance of 3.0633 (11) Å suggests weaker metal bonding between  $\text{Ag}^{\text{I}}$  ions.

## Related literature

For general background, see Akerström (1959); Zhang *et al.* (2002); Liu *et al.* (2006); Song *et al.* (2006). For related structures, see: Yin *et al.* (2007); Anacker-Eickhoff *et al.* (1982); Li *et al.* (2005); Greenwood & Earnshaw (1989). For synthesis, see: Fan *et al.* (2004). For related literature, see: Tang *et al.* (2004).



## Experimental

### Crystal data

$[\text{Ag}(\text{C}_{15}\text{H}_{14}\text{NS}_2)]$   $a = 15.6505$  (19) Å  
 $M_r = 380.26$   $c = 5.0120$  (14) Å  
Trigonal,  $P3_1$   $V = 1063.2$  (3) Å<sup>3</sup>

$Z = 3$   
Mo  $K\alpha$  radiation  
 $\mu = 1.70$  mm<sup>-1</sup>

$T = 293$  (2) K  
 $0.15 \times 0.10 \times 0.10$  mm

### Data collection

Bruker SMART APEXII CCD  
area-detector diffractometer  
Absorption correction: multi-scan  
(SADABS; Sheldrick, 2002)  
 $T_{\text{min}} = 0.785$ ,  $T_{\text{max}} = 0.848$

7409 measured reflections  
2500 independent reflections  
1519 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.094$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.080$   
 $S = 1.00$   
2500 reflections  
172 parameters  
1 restraint

H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.46$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.41$  e Å<sup>-3</sup>  
Absolute structure: Flack (1983),  
with 1227 Friedel pairs  
Flack parameter: 0.07 (5)

**Table 1**

Selected bond lengths (Å).

C1–N1	1.336 (9)	S1–Ag1	2.478 (2)
C1–S2	1.720 (8)	S2–Ag1	3.010 (2)
C1–S1	1.734 (8)	S2–Ag1 <sup>ii</sup>	2.860 (2)
S1–Ag1 <sup>i</sup>	2.446 (2)	Ag1–Ag1 <sup>i</sup>	3.0633 (11)

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

Data collection: *APEX2* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2287).

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**supplementary materials**

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## Poly[( $\mu_3$ -*N,N*-dibenzylthiocarbamato- $\kappa^4$ S,S':S:S')silver(I)]

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### Comment

Synthesis and crystal structure of the Ag(I) complexes with dialkyldithiocarbamates have been widely studied owing to variable coordination configurations since the first description by Akerström (1959). Monomeric, dimeric, hexameric and polymeric structure *etc* in the Ag(I) complexes have been reported in the past decade years, which was indicated that differently substituted alkyl groups and reaction conditions may play crucial roles in the formation of a variety of complexes with unprecedented structures (Zhang *et al.*, 2002; Liu *et al.*, 2006; Song *et al.*, 2006). We have maintained an interest in silver(I)-dithiocarbamate complexes and report herein the structure of the title compound, [(AgC<sub>15</sub>H<sub>14</sub>NS<sub>2</sub>)<sub>3</sub>]<sub>n</sub>.

In the solid state, the title complex has a one-dimensional chain-like polymeric structure and the each repeated Ag(I) units consists of three silver(I) cations and three ligand anions (Fig. 1). Each Ag(I) cation is coordinated with four sulfur atoms from three *N,N*-dibenzylthiocarbamate (DBTC) ligands and shown as a distorted tetrahedral coordination environment. There are two types of sulfur atoms: S1 and the symmetry equivalents are acting as bridges between each two silver atoms with Ag—S distances of 2.446 (1) and 2.478 (2) Å (Table 1). On the other hand, the distances between the Ag(I) atoms and the S2 atoms (2.860 and 3.010 Å) are appreciably different, and both are much longer than the Ag—S(dithiocarbamate) distances [2.5–2.6 Å] (Song *et al.*, 2006; Yin *et al.*, 2007), but smaller Ag1—C1—S1 angles of 94.92° suggests the weaker Ag1—S2 bonding in the compound, as pointed out by Li *et al.* (2005). This agrees with the related compounds reported previously [Anacker-Eickhoff *et al.*, 1982; Song *et al.*, 2006]. Thus the DBTC displays both roles of chelating ligand and *asym*-bridging ligand.

The Ag—Ag distances between adjacent Ag<sup>I</sup> ions are 3.0633 (11) Å, which are longer than 2.886 Å found in metallic Ag (Greenwood *et al.*, 1989) but shorter than the sum of the van der Waals radii of Ag atoms. This may suggest the existence of the weaker metal bonding between Ag<sup>I</sup> ions (Tang *et al.*, 2004). So multi-dentate bridging coordination modes of the chelating ligands and the argentophilic Ag—Ag interactions linked in the [(AgC<sub>15</sub>H<sub>14</sub>NS<sub>2</sub>)<sub>3</sub>] units leads to formation of the one-dimensional chain-like coordination polymer (Fig. 2).

### Experimental

The title compound was prepared by the reaction of AgNO<sub>3</sub> (0.170 g, 1.0 mmol), sodium *N,N*-dibenzylthiocarbamate (NaDBTC) (0.296 g, 2.0 mmol) (Fan *et al.*, 2004) and anhydrous methanol (7 ml) in a 15 ml Teflon liner sealed in a Parr autoclave. The autoclave was placed in a programmable furnace and heated to 353 K for 2 days. Yellow crystals were obtained after cooling to room temperature at 5 K.h<sup>-1</sup> (yield 50%). The compound is hardly soluble in general organic solvent.

## Refinement

All H atoms were placed in calculated positions with C—H = 0.93 Å (aromatic) and 0.97 Å (methylene) and refined in riding mode with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

## Figures

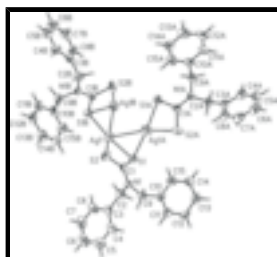


Fig. 1. The molecular structure of the title compound with 50% probability displacement ellipsoids.



Fig. 2. The packing diagram of the title compound viewed down the *b* axis (H atoms have been omitted for clarity).

## Poly[( $\mu_3$ -*N,N*-dibenzylthiocarbamato- $\kappa^4$ S,S':S:S')silver(I)]

### Crystal data

[Ag(C <sub>15</sub> H <sub>14</sub> NS <sub>2</sub> )]	$Z = 3$
$M_r = 380.26$	$F_{000} = 570$
Trigonal, $P3_1$	$D_x = 1.782 \text{ Mg m}^{-3}$
Hall symbol: P 31	Melting point = 491–492 K
$a = 15.6505 (19) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 15.6505 (19) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$c = 5.0120 (14) \text{ \AA}$	Cell parameters from 2450 reflections
$\alpha = 90^\circ$	$\theta = 2.4\text{--}25.0^\circ$
$\beta = 90^\circ$	$\mu = 1.70 \text{ mm}^{-1}$
$\gamma = 120^\circ$	$T = 293 (2) \text{ K}$
$V = 1063.2 (3) \text{ \AA}^3$	Block, yellow
	$0.15 \times 0.10 \times 0.10 \text{ mm}$

### Data collection

Bruker SMART APEXII CCD area-detector diffractometer	2500 independent reflections
Radiation source: fine-focus sealed tube	1519 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.094$
$T = 293(2) \text{ K}$	$\theta_{\text{max}} = 25.2^\circ$
$\varphi$ and $\omega$ scans	$\theta_{\text{min}} = 1.5^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$h = -18 \rightarrow 18$

$T_{\min} = 0.785$ ,  $T_{\max} = 0.848$   
7409 measured reflections

$k = -18 \rightarrow 18$   
 $l = -6 \rightarrow 6$

### Refinement

Refinement on  $F^2$

Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full

H-atom parameters constrained

$R[F^2 > 2\sigma(F^2)] = 0.045$

$w = 1/[\sigma^2(F_o^2)]$   
where  $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2) = 0.080$

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

$S = 1.00$

$\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$

2500 reflections

$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

172 parameters

Extinction correction: none

1 restraint

Absolute structure: Flack (1983), with 1227 Friedel pairs

Primary atom site location: structure-invariant direct methods

Flack parameter: 0.07 (5)

Secondary atom site location: difference Fourier map

### Special details

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

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.0066 (5)	0.2099 (6)	0.5559 (15)	0.0355 (19)
C2	1.0318 (6)	0.3398 (6)	0.8847 (15)	0.043 (2)
H2A	0.9870	0.3301	1.0303	0.051*
H2B	1.0825	0.3273	0.9528	0.051*
C3	1.0786 (5)	0.4436 (6)	0.7943 (16)	0.039 (2)
C4	1.0607 (7)	0.5107 (7)	0.9319 (19)	0.053 (2)
H4	1.0165	0.4894	1.0739	0.064*
C5	1.1086 (8)	0.6088 (7)	0.857 (2)	0.067 (3)
H5	1.0963	0.6529	0.9504	0.081*
C6	1.1742 (7)	0.6428 (7)	0.646 (2)	0.069 (3)
H6	1.2070	0.7092	0.6005	0.083*
C7	1.1905 (7)	0.5768 (8)	0.506 (2)	0.064 (3)
H7	1.2335	0.5980	0.3613	0.077*

## supplementary materials

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C8	1.1424 (7)	0.4788 (6)	0.5810 (17)	0.051 (2)
H8	1.1537	0.4347	0.4835	0.062*
C9	0.8849 (6)	0.2674 (6)	0.5893 (16)	0.041 (2)
H9A	0.8627	0.2342	0.4187	0.049*
H9B	0.8997	0.3350	0.5667	0.049*
C10	0.8041 (6)	0.2174 (6)	0.7892 (17)	0.040 (2)
C11	0.7728 (6)	0.2713 (7)	0.9324 (17)	0.050 (2)
H11	0.8028	0.3389	0.9036	0.059*
C12	0.6973 (6)	0.2274 (7)	1.1197 (18)	0.054 (3)
H12	0.6766	0.2649	1.2147	0.065*
C13	0.6544 (7)	0.1282 (8)	1.161 (2)	0.060 (3)
H13	0.6040	0.0976	1.2853	0.072*
C14	0.6844 (6)	0.0740 (7)	1.0219 (19)	0.052 (3)
H14	0.6539	0.0063	1.0515	0.063*
C15	0.7590 (7)	0.1168 (6)	0.8386 (18)	0.052 (2)
H15	0.7794	0.0785	0.7471	0.062*
N1	0.9764 (4)	0.2672 (4)	0.6704 (13)	0.0360 (16)
S1	0.93514 (15)	0.12847 (14)	0.3071 (5)	0.0439 (5)
S2	1.11785 (16)	0.21987 (18)	0.6397 (5)	0.0543 (7)
Ag1	1.07051 (5)	0.10767 (5)	0.12225 (17)	0.0688 (3)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.023 (4)	0.036 (5)	0.045 (5)	0.012 (4)	0.005 (4)	0.006 (4)
C2	0.050 (6)	0.040 (5)	0.032 (5)	0.018 (5)	0.000 (4)	-0.012 (4)
C3	0.036 (5)	0.038 (5)	0.038 (5)	0.016 (4)	-0.006 (4)	0.006 (4)
C4	0.051 (5)	0.039 (6)	0.060 (6)	0.016 (5)	0.002 (5)	0.004 (5)
C5	0.081 (8)	0.054 (7)	0.073 (8)	0.038 (6)	-0.014 (7)	-0.012 (6)
C6	0.056 (7)	0.047 (7)	0.085 (9)	0.010 (6)	-0.007 (6)	0.022 (6)
C7	0.050 (6)	0.067 (7)	0.056 (7)	0.015 (6)	0.001 (5)	0.016 (6)
C8	0.063 (6)	0.034 (5)	0.047 (6)	0.016 (5)	-0.005 (5)	0.008 (5)
C9	0.046 (5)	0.035 (5)	0.048 (6)	0.024 (4)	0.004 (5)	0.008 (4)
C10	0.038 (5)	0.053 (6)	0.040 (5)	0.032 (5)	-0.003 (4)	0.010 (5)
C11	0.044 (5)	0.057 (6)	0.057 (6)	0.033 (5)	0.009 (5)	0.009 (5)
C12	0.057 (6)	0.067 (7)	0.061 (7)	0.048 (6)	0.018 (5)	0.006 (5)
C13	0.056 (6)	0.071 (7)	0.058 (7)	0.037 (6)	0.020 (5)	0.017 (6)
C14	0.041 (6)	0.040 (5)	0.071 (7)	0.016 (5)	0.001 (5)	0.008 (5)
C15	0.063 (6)	0.050 (6)	0.048 (6)	0.033 (5)	0.008 (5)	0.006 (5)
N1	0.034 (4)	0.033 (4)	0.045 (4)	0.019 (3)	0.003 (4)	0.004 (3)
S1	0.0467 (14)	0.0406 (13)	0.0462 (13)	0.0232 (12)	0.0014 (11)	0.0026 (12)
S2	0.0424 (14)	0.0696 (18)	0.0624 (17)	0.0367 (14)	0.0043 (12)	0.0062 (14)
Ag1	0.0639 (5)	0.0686 (6)	0.0880 (5)	0.0438 (5)	0.0161 (5)	-0.0017 (5)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

C1—N1	1.336 (9)	C9—H9B	0.9700
C1—S2	1.720 (8)	C10—C11	1.370 (11)
C1—S1	1.734 (8)	C10—C15	1.387 (10)

C2—C3	1.480 (10)	C11—C12	1.392 (11)
C2—N1	1.487 (9)	C11—H11	0.9300
C2—H2A	0.9700	C12—C13	1.365 (11)
C2—H2B	0.9700	C12—H12	0.9300
C3—C8	1.376 (10)	C13—C14	1.350 (12)
C3—C4	1.398 (12)	C13—H13	0.9300
C4—C5	1.381 (13)	C14—C15	1.369 (11)
C4—H4	0.9300	C14—H14	0.9300
C5—C6	1.380 (13)	C15—H15	0.9300
C5—H5	0.9300	S1—Ag1 <sup>i</sup>	2.446 (2)
C6—C7	1.375 (13)	S1—Ag1	2.478 (2)
C6—H6	0.9300	S2—Ag1	3.010 (2)
C7—C8	1.381 (12)	S2—Ag1 <sup>ii</sup>	2.860 (2)
C7—H7	0.9300	Ag1—S1 <sup>iii</sup>	2.446 (2)
C8—H8	0.9300	Ag1—S2 <sup>iv</sup>	2.860 (2)
C9—N1	1.489 (9)	Ag1—Ag1 <sup>iii</sup>	3.0633 (11)
C9—C10	1.493 (10)	Ag1—Ag1 <sup>i</sup>	3.0633 (11)
C9—H9A	0.9700		
N1—C1—S2	121.1 (6)	C11—C10—C9	119.9 (8)
N1—C1—S1	119.2 (6)	C15—C10—C9	122.1 (8)
S2—C1—S1	119.6 (5)	C10—C11—C12	121.8 (8)
C3—C2—N1	113.4 (6)	C10—C11—H11	119.1
C3—C2—H2A	108.9	C12—C11—H11	119.1
N1—C2—H2A	108.9	C13—C12—C11	118.4 (8)
C3—C2—H2B	108.9	C13—C12—H12	120.8
N1—C2—H2B	108.9	C11—C12—H12	120.8
H2A—C2—H2B	107.7	C14—C13—C12	120.7 (9)
C8—C3—C4	117.5 (8)	C14—C13—H13	119.7
C8—C3—C2	122.6 (8)	C12—C13—H13	119.7
C4—C3—C2	119.9 (8)	C13—C14—C15	121.1 (9)
C5—C4—C3	120.0 (9)	C13—C14—H14	119.4
C5—C4—H4	120.0	C15—C14—H14	119.4
C3—C4—H4	120.0	C14—C15—C10	120.1 (8)
C6—C5—C4	121.5 (10)	C14—C15—H15	120.0
C6—C5—H5	119.3	C10—C15—H15	120.0
C4—C5—H5	119.3	C1—N1—C2	123.8 (6)
C7—C6—C5	119.0 (9)	C1—N1—C9	123.2 (6)
C7—C6—H6	120.5	C2—N1—C9	113.0 (6)
C5—C6—H6	120.5	C1—S1—Ag1 <sup>i</sup>	107.1 (3)
C6—C7—C8	119.5 (9)	C1—S1—Ag1	94.9 (3)
C6—C7—H7	120.3	Ag1 <sup>i</sup> —S1—Ag1	76.92 (6)
C8—C7—H7	120.3	C1—S2—Ag1 <sup>ii</sup>	102.2 (2)
C3—C8—C7	122.6 (9)	S1 <sup>iii</sup> —Ag1—S1	171.87 (8)
C3—C8—H8	118.7	S1 <sup>iii</sup> —Ag1—S2 <sup>iv</sup>	85.02 (8)
C7—C8—H8	118.7	S1—Ag1—S2 <sup>iv</sup>	102.21 (7)
N1—C9—C10	112.3 (6)	S1 <sup>iii</sup> —Ag1—Ag1 <sup>iii</sup>	52.01 (6)

## supplementary materials

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N1—C9—H9A	109.1	S1—Ag1—Ag1 <sup>iii</sup>	123.76 (6)
C10—C9—H9A	109.1	S2 <sup>iv</sup> —Ag1—Ag1 <sup>iii</sup>	88.38 (5)
N1—C9—H9B	109.1	S1 <sup>iii</sup> —Ag1—Ag1 <sup>i</sup>	120.83 (6)
C10—C9—H9B	109.1	S1—Ag1—Ag1 <sup>i</sup>	51.07 (5)
H9A—C9—H9B	107.9	S2 <sup>iv</sup> —Ag1—Ag1 <sup>i</sup>	140.89 (5)
C11—C10—C15	118.0 (8)	Ag1 <sup>iii</sup> —Ag1—Ag1 <sup>i</sup>	86.91 (2)

Symmetry codes: (i)  $-y+1, x-y-1, z+1/3$ ; (ii)  $x, y, z+1$ ; (iii)  $-x+y+2, -x+1, z-1/3$ ; (iv)  $x, y, z-1$ .



Fig. 1

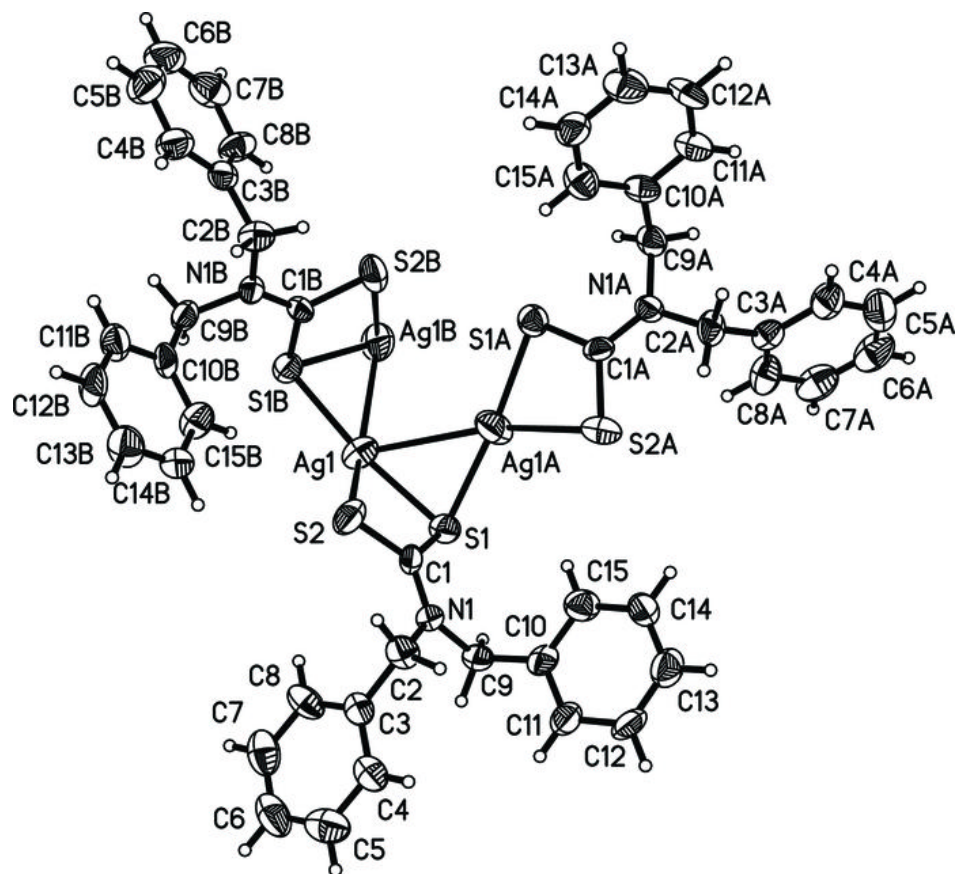


Fig. 2

