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The Intertwined Double-(–Ag–SR–)$_\infty$-Strand Chain Structure of Crystalline (3-Methylpentane-3-thiolato)silver, in Relation to (AgSR)$_8$ Molecules in Solution

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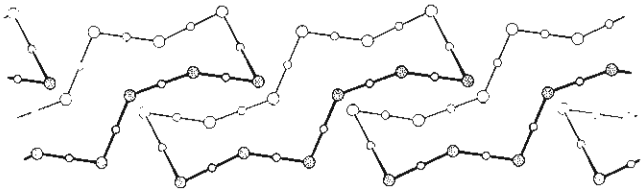
Received January 4, 1983

Crystalline (3-methylpentane-3-thiolato)silver is one-dimensionally nonmolecular. Silver and sulfur atoms constitute the cores of chains, which are approximately linear and well separated from each other by the alkyl substituents that radiate from the chains. Each *chain* contains two separate *strands*, each with alternating silver atoms and doubly bridging thiolate ligands. All silver atoms are approximately linearly coordinated (S–Ag–S range 169–178°). A structural feature unprecedented in homoleptic silver thiolate structures is the absence of any secondary silver–sulfur bonding. Each strand contains approximately planar zigzag S–Ag–S–Ag–S–Ag–S segments, which are connected at their ends by single silver atoms linking segments on one side of the chain to parallel segments on the opposite side of the chain. The two strands of the chain thereby wind around each other at every fourth silver atom (the *a* repeat of the crystal) without interstrand bonding. The closest contact between strands is Ag--Ag = 2.886 (4) Å, which is interpreted as nonbonding. A straightforward mechanism for interconversion of the *nonmolecular* crystal structure and the *molecular* (AgSR)$_8$ structure in benzene solution is proposed. A zigzag cyclic structure for (AgSR)$_8$ is postulated on the basis of the crystal structure. Approximately 8% slip-faulting of the chains has been observed and modeled for one of the two crystals investigated. Crystal data: $C_{48}H_{104}Ag_8S_8$, M_r 1800.8; a = 12.105 (2), b = 14.289 (2), c = 19.539 (3) Å; α = 85.77 (1), β = 87.77 (1), γ = 86.30 (1)°; Z = 2; space group $P\bar{1}$, Cu Kα, 1878 observed reflections, R = 0.061.

Introduction

Compounds AgSR have been known and used for a long time, but with little definitive information about their structures. Åkerström[1] has prepared a considerable number of silver alkane- and cycloalkanethiolates, (AgSR)$_n$, and measured their molecular weights in solution, which led him to recognize a relationship between their molecularity and molecular size (n) and the degree of branching at the α-carbon atom. When R is a tertiary alkyl, n is 8, and when R is a secondary alkyl, n is 12. With R = cyclohexyl, the molecular weight was less reliable, and indicated $n \sim 25$. Silver primary alkanethiolates are either insoluble or slowly soluble, yielding unreliable high molecular weights in solution, indicative of nonmolecular crystal structure.

The crystal structure of (cyclohexanethiolato)silver (**1**) was determined by Hesse et al.[2] and described as a one-dimensionally nonmolecular silver–sulfur framework shielded from its neighbors by the cyclohexyl substituents. However, examination of the details of this crystal structure has led to reinterpretation[3] of it in terms of (AgSR)$_{12}$ cyclic molecules, which are lapped over each other along the chain. Some secondary (longer) Ag--S bonding occurs between the cyclic molecules and there are two contracycle secondary Ag--S interactions, as would be expected for a 24-membered ring with no conformational stability.



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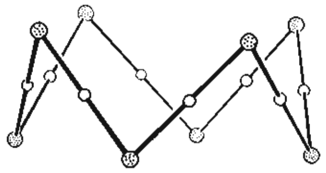
From these findings a reasonable hypothesis is that (AgSR^{sec})$_{12}$ molecules are cyclic, like **1**, and that (AgSR^{tert})$_8$ molecules are also cyclic, as 16-membered rings with linear twofold coordination of silver. A reasonable structure postulated for (AgSR^{tert})$_8$ is **2**, which is part of the playpen structure **3** known for [$Ni_8(SCH_2COOC_2H_5)_{16}$].[4]



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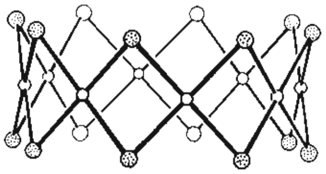

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We have prepared some of the compounds studied by Åkerström,[1] in order to determine crystal structures, to interpret them in terms of probable molecular structures in solution, and to evaluate our proposed structure **2**. In this paper we describe our work with (3-methylpentane-3-thiolato)silver (**4**), containing a tertiary alkanethiolate.

Results

Unlike less branched compounds, **4** is readily soluble in carbon tetrachloride, chloroform, benzene, toluene, heptane, petroleum ether, ether, tetrahydrofuran, warm acetone, and warm alcohols. Crystallization by various methods yielded soft colorless crystals, usually with growth pronounced along one axis, but also with empty pits and channels collinear with the needle axis. The best crystals were obtained from butanol, and were used for the diffraction measurements, although they were not ideal.

Crystal Structure. The structure is one-dimensionally nonmolecular, along the a (needle) axis of the crystals. Unbranched chains of silver and sulfur atoms are surrounded by the tertiary alkyl substituents, which keep the chains well separated. The distances (S---S) between nearest chains are ca. 7.5, 9.5 Å. The centers of symmetry in the triclinic cell are located between, not within, the chains.

The interesting part of the structure is within the chains. Figure 1 shows that each *chain* contains two separate and

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[1] (a) Åkerström, S. *Acta Chem. Scand.* **1964**, *18*, 1308. (b) Åkerström, S. *Ark. Kemi* **1965**, *24*, 505.

[2] Hong, S.; Olin, A.; Hesse, R. *Acta Chem. Scand., Ser. A* **1975**, *A29*, 583.

[3] Dance, I. G. *Inorg. Chim. Acta* **1977**, *25*, L17.

[4] Dance, I. G.; Scudder, M. L.; Secomb, R., submitted for publication.

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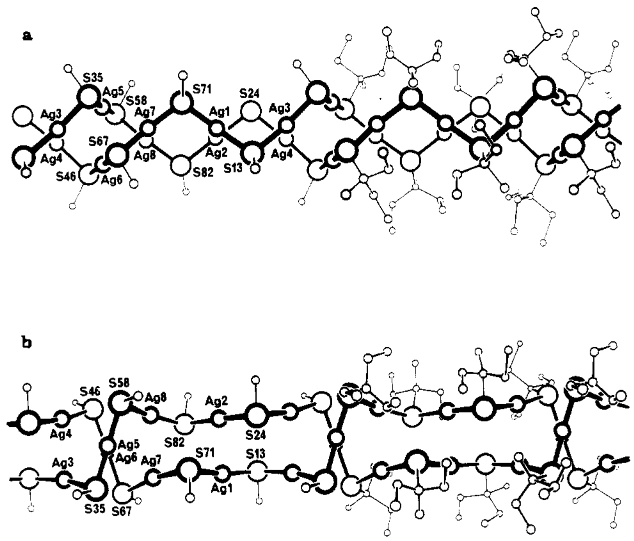
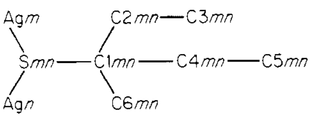


Figure 1. Perpendicular view of the double-strand chain of AgSC$(CH_3)(C_2H_5)_2$ (**4**): (a) view almost normal to the pseudoplanar zigzag segments, with open and full bonds to distinguish the separate strands; (b) view perpendicular to that in (a) showing the planar segments of the strands and the crossover at Ag5, Ag6. In the left half (one unit cell repeat) the Ag and S atoms are labeled and the ligand C_α atoms only are shown.

unconnected $(-Ag-SR-)_\infty$ *strands*. Each strand contains an approximately planar zigzag (Figure 1a) segment extending for three linearly coordinated silver atoms, these segments being approximately parallel in the two strands (Figure 1b). In fact, each chain can be envisaged as possessing two planes. Each strand of the chain has an Ag_3 segment in one plane and then twists out of that plane through a linearly coordinated silver atom (Ag5 or Ag6) to the next Ag_3 segment, which lies in the other plane. Each strand twists at the same position along the chain, so that the two spiral strands are entwined without any bonding between them.

The strands are not crystallographically independent. The sequence along any strand is –[Ag7′–Ag1–Ag3]–(Ag5)–[Ag8–Ag2′–Ag4′]–(Ag6′)–, where square brackets enclose the planar segments connected by Ag5, Ag6 in the twist segments and the primes indicate atoms in a different asymmetric unit ($x \pm 1$). Note that the location of the crystallographic centers of inversion is such that within each chain the two strands run in the same direction (as defined by the sequence above) and each chain is chiral, while adjacent chains run in opposite directions. The crystallographic asymmetric unit is that section of the chain within one unit cell repeat along *a*: the repeat distance along one *strand* is 2*a*.

Important distances and angles are given in Table I. Atom labeling[5] is



All S–Ag–S coordination segments are close to linear (S–Ag–S = 173.2°, 3.4°, 8^6), and there are no signfiicant variations in the Ag–S bond length (Ag–S = 2.366 Å, 0.014 Å, 16^6). The Ag–S–Ag angles fall into two classes, those at the sulfur atoms in the planar segments of the strand being 15° larger (102.8°, 2.0, 4^6) than those at the sulfur atoms in the crossover segment of the strand (87.2°, 1.7°, 4^6).

Table I. Selected Bond Distances (Å) and Angles (deg) for AgSC$(CH_3)(C_2H_5)_2$

Ag1–S13	2.34 (1)	Ag5–S58	2.36 (1)
Ag1–S71	2.36 (1)	Ag5–S35	2.37 (1)
Ag2–S24	2.38 (1)	Ag6–S46	2.34 (1)
Ag2–S82	2.38 (1)	Ag6–S67	2.37 (1)
Ag3–S35	2.38 (1)	Ag7–S71	2.36 (1)
Ag3–S13	2.36 (1)	Ag7–S67	2.38 (1)
Ag4–S24	2.35 (1)	Ag8–S82	2.37 (1)
Ag4–S46	2.38 (1)	Ag8–S58	2.38 (1)
S13–C113	1.88 (5)	S58–C158	1.95 (4)
S24–C124	1.96 (7)	S67–C167	1.84 (5)
S35–C135	1.88 (5)	S71–C171	1.91 (4)
S46–C146	1.89 (4)	S82–C182	1.90 (5)
S13–Ag1–S71	171.8 (4)	S58–Ag5–S35	177.3 (3)
S24–Ag2–S82	176.1 (4)	S46–Ag6–S67	177.7 (5)
S35–Ag3–S13	169.2 (4)	S71–Ag7–S67	170.0 (4)
S24–Ag4–S46	170.2 (4)	S82–Ag8–S58	173.0 (5)
Ag1–S13–Ag3	104.2 (5)	Ag5–S58–Ag8	85.9 (4)
Ag2–S24–Ag4	104.7 (5)	Ag6–S67–Ag7	85.6 (4)
Ag3–S35–Ag5	87.9 (4)	Ag7–S71–Ag1	101.4 (5)
Ag4–S46–Ag6	89.2 (4)	Ag8–S82–Ag2	100.8 (4)

Table II. Silver–Silver Atom Distances (Å) in AgSC$(CH_3)(C_2H_5)_2$

(a) Distances between Opposing Silver Atoms on Different Strands, in Comparison with the Distances between the Midpoints of Their Pairs of Coordinated Sulfur Atoms

Ag1--Ag2	2.886 (4)	$\overline{S13,S71}$--$\overline{S24,S82}$	2.66
Ag3--Ag4	3.202 (5)	$\overline{S13,S35}$--$\overline{S24,S46}$	3.58
Ag5--Ag6	3.151 (4)	$\overline{S35,S58}$--$\overline{S46,S67}$	3.25
Ag7--Ag8	3.313 (5)	$\overline{S67,S71}$--$\overline{S58,S82}$	3.58

(b) Additional Contacts at the Crossover Region

Ag3--Ag5	3.295 (5)	Ag5--Ag7	3.359 (5)
Ag3--Ag6	3.248 (5)	Ag5--Ag8	3.227 (5)
Ag4--Ag5	3.258 (5)	Ag6--Ag7	3.224 (4)
Ag4--Ag6	3.314 (5)	Ag6--Ag8	3.308 (5)

Pseudopyramidal stereochemistry occurs at all sulfur atoms, the mean value of the inclination of the S*mn*–C1*mn* vector to the Ag*m*–S*mn*–Ag*n* plane being 64.6°. Individual values of this inclination for ligands *mn*: 13, 60.3; 24, 71.8°; 35, 67.5°; 46, 62.2°; 58, 63.4°; 67, 63.7°; 71, 65.8°; 82, 62.2°. There is no correlation of this S*mn*–C1*mn* inclination angle with the two classes of Ag*m*–S*mn*–Ag*n* angles. The configuration at each sulfur atom is such that the substituent is directed away from the central axis of the chain.

The shortest contacts between the strands of the chain are Ag--Ag, not Ag--S. The Ag--Ag distances across the central axis of the chain are given in Table II, in comparison with the distances between midpoints of the pairs of sulfur atoms bound to each silver. These values, and Figure 1b, show that the displacements from linear coordination at the silver atoms are greatest in the planar zigzag segments of the strands and that these deviations occur symmetrically; Ag1 and Ag2 are displaced outside their respective S--S lines, while Ag7 and Ag8, and Ag3 and Ag4, are displaced toward each other, inside the S--S lines. Despite this systematic effect to lengthen the shortest separation (Ag1--Ag2) of the strands, and to shorten the longer separations, the Ag1--Ag2 distance, 2.886 Å, is still distinctly shorter than all other Ag--Ag distances.

The distances in Table II also show that at the crossover region six silver atoms, Ag3 to Ag8, constitute a pair of Ag_4 tetrahedra sharing the common Ag5--Ag6 edge.

Some of the carbon atoms are poorly defined in the crystal. The mean C–C distance is 1.54 Å, and the standard deviation of the sample of 43 is 0.17 Å.

Discussion

Solution and Crystal Structures. Åkerström's ebullioscopic determinations of the molecular weight of **4** in benzene at concentrations of 2.1, 3.3, 4.7, and 5.6 wt % yielded values

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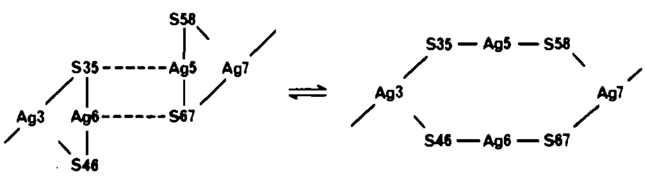
(5) In ligand *mn* = 35 there are alternative (disordered) positions for C5, while in ligands *mn* = 46, 58 there is disorder between methyl and ethyl groups attached to C1.

(6) Values quoted are the mean, estimated standard deviation, and size of the *sample*.

1805, 1825, 1750, and 1780, in good agreement with the calculated molecular weight of 1801 for the octameric formula $(AgSR)_8$.[1] It appears unlikely that the measured values represent averages for differently sized molecules in solution. The question then arises as to the mechanism of interconversion of the nonmolecular structure in the solid state and the octameric molecule in benzene solution. The occurrence of eight AgSR units in the crystallographic asymmetric unit supports the probability of direct transfer of an octameric molecule between solid and solution phases. However the complete absence of Ag--S secondary bonding in the crystal allows no clue to the identity of the eight AgSR units. The straightforward analysis that was made[3] for crystalline **1** in terms of secondary Ag--S bonding cannot be made for **4**. The relationship between the molecular $(AgSR)_8$ and nonmolecular $(AgSR)_\infty$ structures of **4** involves bond breaking and making, of which there is no trace of residual interaction in the crystal structure.

Nevertheless, there is a clear mechanism by which the interchange can occur at the crossover region. The mechanism involves end-to-end association of cyclic octameric molecules, as shown in **5**, and concerted interchange of Ag–S bonds to give **6**, the crossover section of the crystal. In this way the crossover section, which is not a necessary component of a nonmolecular structure with parallel strands, is regarded as the remnant of, and evidence for, the cyclic octameric molecules. The zigzag segments in the crystal structure also support the postulated puckered ring conformation **2** for $(AgSR)_8$.



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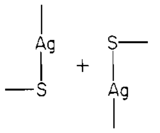
The postulated mode of association, **5**, has been observed in the crystal structure of $[Ag_6(SPh)_8]_2^{4-}$.[7]



Chain Structure. There is evidence of slip-faulting of the chains, parallel to *a*, mounting to about 8% of the structure in one of the crystals examined. This faulting, detailed in the Experimental Section and in the Appendix,[10] is not surprising as the isolated chains in the crystal are hydrocarbon coated and loosely packed. The chain structure of the crystal accounts also for (i) the predominant crystal growth and cleavage along the *a* axis, (ii) the frequent occurrence of empty channels parallel to the chain axis, which would be due to preferential growth at promontory chains, and (iii) the softness of the crystals.

A needle habit is characteristic of crystalline AgSR compounds. Both **1** and **4** have one-dimensional structures with radiating substituents: **1** is columnar, with four AgSR strands in cross section, while **4** has two strands per chain. It seems very likely that similar structures will be found in many related compounds. Hesse[2] mentions unpublished work on an unlimited chain structure for crystalline (2,3-dimethylbutane-2-thiolato)silver. Only when R is extremely bulky, is it likely that a single $(AgSR)_\infty$ strand would constitute the chain.

In the two structures **1** and **4** with more than one strand there are two quite different relationships between the strands. In **1** there are secondary Ag–S bonds, which occur between the overlapped cyclic $(AgSR)_{12}$ molecules: in **4** the strands wind around each other with no secondary Ag–S bonding.

The Ag,S framework of **4** is regular, with virtual symmetry higher than the crystallographic symmetry. This could be derived from rigidity in the cyclic molecule $(AgSR)_8$ (**2**). It is unlikely that the substituents influence the Ag,S structure, as they are not tightly packed and are partly disordered.

Silver–Silver Interaction. The closest contact between the strands of the chain is Ag1···Ag2, at a distance (2.886 Å) that is equal to the interatomic separation in silver metal.[8] Our interpretation of this contact is that it represents the onset of a repulsive interaction between nonbonded silver atoms. In this structure the linear geometry at silver indicates that its bonding is fulfilled by the two thiolates, and there is no requirement for secondary silver–sulfur bonding. The slight bending of Ag1 and Ag2 outside their S--S lines, away from each other, is indicative of weak repulsion, not attraction, between them. We consider that the two zigzag strands of the chain approach each other until limited by the internal repulsion between opposite silver atoms.

A corollary of this hypothesis is a strong dependence of both the capacity and the radius for silver–silver bonding on the coordination number and nature of other ligands. Twelve-coordinate silver with no other ligands *bonds* with silver at 2.88 Å, while two-coordinate silver with anionic thiolate ligands is *nonbonding* with silver at the same distance.

Structure–Color Relationship. Crystalline compounds AgSR are either colorless or yellow. All silver thiolates containing trigonal silver, from either primary[7,9] or secondary[2,3] coordination, are yellow, while **4**, which contains only digonal silver, it colorless. Of the other (alkanethiolato)silver compounds for which structures are not yet confirmed, all $AgSR^{tert}$ are colorless and all except one $AgSR^{sec}$ are yellow.[1] A reasonable hypothesis is that absorption due to charge-transfer from thiolate to linearly coordinated silver occurs at higher energy than that to trigonally coordinated silver.

Experimental Section

The preparation of 3-methylpentane-3-thiol followed the method of Akerström.[1b] To a stirred mixture of 3-methyl-3-pentanol (51 g, 61 mL, 0.5 mol) and thiourea (46.5 g, 0.6 mol) was added 48% hydrobromic acid (123.1 g, 82.5 mL, 0.7 mol) over 20 min. After refluxing for 30 min, the mixture was cooled to room temperature. The aqueous layer was separated and to it was added aqueous 5 M sodium hydroxide solution (30 mL), and the mixture was distilled with stirring over 45 min. The upper layer of the distillate was separated, dried over anhydrous sodium sulfate, and distilled at 62–65 °C (90 mm) to give 3-methyl-3-pentanethiol; 43.14 g, 73%. ^{1}H NMR ($CDCl_3$): m, 5, δ 1.83–1.37, $-CH_2-$ and –SH (peak at δ 1.38 exchanges with D_2O); s, 3, δ 1.25, $-S-C-CH_3$; m, 6, δ 1.13–0.70, $-CH_2CH_3$.

The silver derivative, **4**, was precipitated by addition of silver nitrate in water to a solution of the thiol in acetone. After collection, the precipitate was washed with a small amount of cold acetone and vacuum dried; yield 100%. The product is slightly soluble in acetonitrile and soluble in carbon tetrachloride, chloroform, benzene, toluene, heptane, petroleum ethers, warm acetone, ether, and THF and in butanol, 2-propanol, and ethanol warmed to 50°. Recyrstallization was effected from (i) butanol, (ii) acetone, (iii) acetone/ethanol, or (iv) heptane. Anal. Calcd for $AgSC_6H_{13}$: C, 32.02; H, 5.82. Found: C, 31.88; H, 6.12. ^{1}H NMR; q, 4, δ 1.74, $-CH_2-$; s, 3, δ 1.42, $-S-C-CH_3$; t, 6, δ 0.98, $-CH_2CH_3$. Mp: 145–146 °C (lit.[1b] mp 146.5–148.0 C).

All of the crystallization methods noted above yielded colorless crystals with a needle or prismatic habit and with pronounced occurrence of empty pits and channels parallel to the needle axis. In many cases there was multiple growth enclosing a central cavity. The

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(7) Dance, I. G. *Inorg. Chem.* **1981**, *20*, 1487.

(8) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Oxford University Press: London, 1975; p 1015.

(9) Dance, I. G. *Aust. J. Chem.* **1978**, *31*, 2195.

Table III. Details of Diffraction Analysis (Crystal A)

formula, mass	$C_{48}H_{104}Ag_8S_8$, 1800.8
cryst descripn	colorless needle fragment; $\{\bar{3}11\}$, $\{011\}$, $\{001\}$
space group	$P\bar{1}$
a/Å	12.105 (2)
b/Å	14.289 (2)
c/Å	19.539 (3)
α/deg	85.77 (1)
β/deg	87.77 (1)
γ/deg	86.30 (1)
d_{calcd}/g cm^{-3}	1.78
temp/°C	21
radiation, λ/Å	Cu Kα, 1.5418
scan mode	$\theta/2\theta$
$2\theta_{max}$/deg	70
μ/cm^{-1}	211.8
cryst dimens/mm	0.20 × 0.07 × 0.08
max, mean, and min transmission coeff	0.307, 0.265, 0.180
no. of intensity measurements	2903
std intensity decay	1 → 0.70
criterion for obsd reflcn	$I/\sigma(I) > 3$
no. of independent obsd reflcns	1878
no. of reflcns (m) and variables (n) in final refinement	1878, 356
$R = \Sigma^m \lvert\Delta F\rvert / \Sigma^m \lvert F_o \rvert$	0.061
$R_w = [\Sigma^m w \lvert\Delta F\rvert^2 / \Sigma^m w \lvert F_o\rvert^2]^{1/2}$	0.076
$[\Sigma^m w \lvert\Delta F\rvert^2/(m-n)]^{1/2}$	2.20

Table IV. Atomic Coordinates (Ag, S Only) for $AgSC(CH_3)(C_2H_5)_2$[10]

atom	x	y	z
Ag1	0.1122 (3)	0.3259 (2)	0.1961 (2)
Ag2	0.1128 (3)	0.1762 (2)	0.3037 (2)
Ag3	0.4186 (3)	0.3268 (2)	0.1906 (2)
Ag4	0.4210 (3)	0.1687 (2)	0.3156 (2)
Ag5	0.6253 (3)	0.1654 (2)	0.2020 (2)
Ag6	0.6091 (3)	0.3281 (2)	0.3030 (2)
Ag7	0.8109 (3)	0.3312 (2)	0.1904 (2)
Ag8	0.8121 (3)	0.1620 (2)	0.3158 (2)
S13	0.2582 (9)	0.3892 (8)	0.2482 (6)
S24	0.2798 (9)	0.1047 (8)	0.2582 (6)
S35	0.5642 (9)	0.2769 (8)	0.1138 (6)
S46	0.5516 (9)	0.2188 (8)	0.3905 (6)
S58	0.6890 (9)	0.0496 (8)	0.2859 (6)
S67	0.6651 (9)	0.4433 (8)	0.2177 (6)
S71	0.9708 (9)	0.2427 (8)	0.1538 (5)
S82	0.9507 (9)	0.2581 (8)	0.3475 (5)

air-stable crystals were soft and were fractured along the needle axis. The best specimens were from butanol, but were not ideal. The crystal used for collection of most of the X-ray diffraction data showed very slight diffraction splitting.

X-ray analysis was made with a CAD4 diffractometer. On exposure to X-rays the crystals turned yellow and the diffraction intensity decayed by about 30% during a period of 2 days. There was no evidence of crystal fragmentation during the X-ray-induced decomposition. Diffraction intensity data were collected in expanding shells using one crystal (A) to $\theta = 35°$ and a second crystal (B) for $35 \leq \theta \leq 45°$. Corrections for crystal decay and for absorption were applied. Numerical details of the crystallographic analysis are provided in Table III.

The structure was solved by using the data from crystal A. During the least-squares and Fourier calculations to locate all of the carbon atoms, several phenomena related to each other were observed: (i) In Fourier maps for crystal A there appeared peaks (about the same size as carbon atom peaks) that were ghosts of silver atom positions, displaced parallel to a. (ii) $|F_o|$ was consistently larger than $|F_c|$ for $0kl$ data from crystal A. (iii) There were branching disorder and conformational disorder in some of the alkyl side chains.[5] (iv) There were appreciable discrepancies between observed structure factors common to the crystal A and crystal B data sets.

It was postulated that slip-faulting of the chains, parallel to a, occurred in crystal A, and this was tested and confirmed by least-squares refinement of data set A using h-index-dependent scale factors (see Appendix[10]). A difficulty arises in that a component of the temperature factor correlates with the scale factors: β_{11} interacts in this fashion since the space group is $P\bar{1}$. Similar investigation of the scale factors for data set B gave no evidence of the h-index dependence found for crystal A.

At this stage it was apparent that there existed two types of disorder in this structure, namely some side chain disorder in both crystals (which were not necessarily the same in this respect) and slip-faulting of the chains in crystal A. However the limited amount and quality of the diffraction data available, particularly from crystal B (16 reflections per atom), would not allow complete description and refinement of the structures of both crystals. Therefore, the following strategy was adopted to achieve the most chemically significant description of the structure. It was first assumed (a) that the silver and sulfur atom positions and anisotropic thermal motion were the same for both crystals, (b) that the disordered carbon atoms, with severely limited contribution to the structure factors, could not be located better than with the lower angle data from crystal A, and (c) that slip-faulting and h-index-dependent scale factors occurred only for crystal A. After preliminary optimization of carbon atom parameters, least-squares refinement using the combined data, with h-index-dependent scale factors for data set A, one scale factor for data set B, and silver and sulfur positional and anisotropic thermal parameters (2948 data, 154 parameters), converged at $R = 0.075$ with no significant systematic discrepancies in structure factors. This combination of data and parameters allowed the scale factors for data set A to be determined without the interference of correlation with β_{11} parameters.[11] With these scale factors fixed, the positions and thermal parameters of all other atoms were refined for crystal A, which had the larger data set and better defined carbon atoms. This final refinement, $R = 0.061$, yielded the structure reported here.[12] A final difference map showed peaks up to +1.2 e Å^{-3}, near the side chains, possibly indicative of subsidiary disorder. Hydrogen atoms were not included.

Scattering factors were from ref 13, with inclusion of anomalous scattering by silver and sulfur.

Silver and sulfur atomic coordinates are listed in Table IV. All other atomic parameters are deposited as supplementary material.[10] The scale factors k for crystal A were determined to be 1.161 (7), 0.928 (5), 0.939 (6), 0.940 (5), 0.962 (7), 0.964 (9), 0.98 (1), 1.03 (2), and 1.05 (3) for $h = 0 \rightarrow 8$, respectively. The systematic increase in $k(h)$, $h = 1 \rightarrow 8$, is not explained. On the basis of the theory outlined in the Appendix,[10] it can be estimated that $1 - (0.974/1.161)^{1/2} = 8\%$ of crystal A is affected by slip-faulting.

Other crystals of this compound, obtained by different methods, were examined on the diffractometer with the object of obtaining better crystals and better diffraction data; the prospects for achieving this end did not appear to be good.

Acknowledgment. This research was supported by the Australian Research Grants Scheme. D. Craig assisted with diffraction data collection.

Registry No. 4, 87337-48-2.

Supplementary Material Available: A tabulation of final atomic parameters (crystal A), listings of F_o and F_c for crystals A and B, a listing of powder diffraction lines, and an Appendix on the diffraction theory for the one-dimensionally slip-faulted structure (16 pages). Ordering information is given on any current masthead page.

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(10) See paragraph at end of paper regarding supplementary material.

(11) Note that this depends on the assumption that crystal B is unfaulted.

(12) The relatively high $R = 0.175$ for data set B with these final parameters is due to the much smaller size of the data set and probably a difference carbon atom disorder in crystal B.

(13) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.