

The Crystal Structure of Silver(I) Cyclohexanethiolate

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The crystal structure of silver(I) cyclohexanethiolate, $\text{AgSC}_6\text{H}_{11}$, has been determined from three-dimensional X-ray data. The crystals are triclinic, space group $P\bar{1}$. The unit cell contains twelve formula units and has the dimensions $a=14.827 \text{ \AA}$, $b=15.747 \text{ \AA}$, $c=11.218 \text{ \AA}$, $\alpha=103.68^\circ$, $\beta=107.71^\circ$, and $\gamma=91.79^\circ$.

The structure consists of infinite silver-sulfur frameworks extending in the c -direction. These frameworks are shielded from each other by the surrounding cyclohexane rings. Both two- and three-coordinated silver atoms are present.

The silver(I) alkanethiolates belong to the same groups of compounds, $(AX)_n$, as the polymeric mono- and dithiocarbamates of Cu(I) ,^{1,2} Ag(I) ,^{3,4} Au(I) ,⁵ and Tl(I) ⁶ which have been studied in this laboratory. These studies have shown the existence of a close relationship between the degree of association n ($=2, 4, \text{ or } 6$) of these substances in inert solvents and in their crystal structures. The preparation and properties of many silver(I) alkanethiolates, Ag(I) SR , has been reported by Åkerström.⁷ Cryoscopic and ebullioscopic molecular weight determinations in benzene and chloroform of most of these compounds showed that they were associated in these solvents. With the sulfur atom bound to a tertiary carbon atom, the degree of association was found to be 8. When the sulfur atom was associated with a secondary carbon atom, n in most cases was close to 12. When R was unbranched, the compounds tended to be so insoluble that molecular weight determinations could not be performed.

X-Ray crystal structure investigations of silver(I) thiolates have been started to obtain information about the structures of polymers with high degree of association in solutions. It was then found that only a few of the thiolates yielded crystals of sufficiently good quality for

single-crystal diffraction studies. In most cases the crystals showed severe disorder or twin formation. We here report our results on silver(I) cyclohexanethiolate. For this compound, which is rather insoluble, a value of $n=25$ was found by Åkerström. This value is thus larger than for most other *sec*-thiolates, which have $n=12$.

EXPERIMENTAL

A sample of silver(I) cyclohexanethiolate was kindly supplied by Dr. S. Åkerström. The unit cell parameters were determined from a powder photograph taken with a Guinier-Hägg focussing camera using $\text{CrK}\alpha$ radiation ($\lambda=2.2896 \text{ \AA}$) and silicon ($a=5.4305 \text{ \AA}$) as an internal standard. The crystal data are presented in Table 1. Using $[001]$ as the rotation axis, equi-inclination photographs were recorded up to $l=9$ with nickel-filtered $\text{CuK}\alpha$ radiation at room

Table 1. Crystal data.

Formula unit: $\text{AgSC}_6\text{H}_{11}$
 Crystal system: triclinic
 Space group: $P\bar{1}$

Unit cell parameters:^a

$a=14.827(3)$ $b=15.747(3)$ $c=11.218(1) \text{ \AA}$
 $\alpha=103.68(1)$ $\beta=107.71(1)$ $\gamma=91.79(1)^\circ$

Formula weight: 223.09

Cell volume: 2409 \AA^3

Number of formula units per unit cell: 12

Density(measured): $1.85(1) \text{ g cm}^{-3}$

Density(calculated): 1.845 g cm^{-3}

Linear absorption coefficient for $\text{CuK}\alpha$: 221 cm^{-1}

^a Here and elsewhere in this paper estimated standard deviations given within parentheses refer to the least significant digits.

temperature. The cross section of the crystal needles averaged 0.04×0.05 mm². The multiple film technique with 5 films was used, and 2154 independent reflexions were collected. The relative intensities were estimated visually.

The crystals decomposed rather rapidly in the X-ray beam, and each crystal was used for

the recording of only one layer. Inter-layer scale factors were determined from small range Weissenberg photographs of the layers recorded on the same film. When the scale factors were later refined in the least-squares treatment of the data, only small changes were observed. The intensity data have been corrected for

Table 2. The final atomic coordinates and thermal parameters with their e.s.d.'s. in parentheses. The anisotropic thermal parameters of the silver and sulfur atoms are given in Table 3.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> Å ²
Ag(1)	-0.0166(2)	0.2354(2)	0.1330(3)	
Ag(2)	0.0969(2)	0.0311(2)	0.1961(3)	
Ag(3)	0.0399(2)	0.1775(2)	0.3785(3)	
Ag(4)	-0.0065(3)	-0.1694(2)	0.1335(3)	
Ag(5)	0.0230(2)	-0.1199(2)	0.4287(3)	
Ag(6)	-0.1171(2)	0.0705(2)	0.1416(3)	
S(A)	0.0860(7)	0.3162(7)	0.3407(10)	
S(B)	-0.0987(8)	-0.2237(8)	0.2474(10)	
S(C)	0.1360(7)	-0.1579(7)	0.0603(9)	
S(D)	0.0898(6)	0.0270(6)	0.4065(8)	
S(E)	0.1186(6)	0.0698(6)	0.0096(8)	
S(F)	-0.1391(7)	0.1299(7)	0.3500(9)	
C(A1)	0.210(3)	0.325(3)	0.338(4)	7(1)
C(A2)	0.274(3)	0.369(3)	0.473(4)	6(1)
C(A3)	0.380(4)	0.376(4)	0.473(5)	10(2)
C(A4)	0.387(4)	0.427(4)	0.368(5)	10(2)
C(A5)	0.321(3)	0.385(3)	0.239(5)	8(1)
C(A6)	0.212(3)	0.375(3)	0.227(4)	8(1)
C(B1)	-0.065(4)	-0.336(4)	0.265(5)	10(1)
C(B2)	-0.046	-0.383	0.139	
C(B3)	0.015	-0.459	0.160	
C(B4)	-0.038	-0.522	0.214	
C(B5)	-0.057	-0.477	0.339	
C(B6)	-0.111(5)	-0.397(5)	0.320(7)	20(2)
C(C1)	0.214(4)	-0.247(4)	0.094(5)	10(1)
C(C2)	0.177(5)	-0.293(5)	0.175(6)	12(2)
C(C3)	0.264(5)	-0.368(4)	0.194(6)	11(2)
C(C4)	0.363(5)	-0.326(5)	0.246(7)	13(2)
C(C5)	0.395(5)	-0.279(5)	0.171(7)	13(2)
C(C6)	0.317(5)	-0.200(4)	0.131(6)	12(2)
C(D1)	0.211(3)	0.046(3)	0.519(3)	5(1)
C(D2)	0.275(3)	-0.030(3)	0.471(3)	5(1)
C(D3)	0.376(4)	-0.013(3)	0.564(5)	8(1)
C(D4)	0.426(4)	0.083(4)	0.587(5)	9(1)
C(D5)	0.360(3)	0.153(3)	0.623(4)	7(1)
C(D6)	0.262(3)	0.137(3)	0.531(4)	7(1)
C(E1)	0.243(3)	0.112(2)	0.065(3)	5(1)
C(E2)	0.279(3)	0.106(3)	-0.051(4)	8(1)
C(E3)	0.387(4)	0.147(3)	-0.002(5)	8(1)
C(E4)	0.440(4)	0.089(4)	0.075(5)	10(1)
C(E5)	0.410(4)	0.106(4)	0.201(6)	11(2)
C(E6)	0.306(4)	0.066(3)	0.155(5)	8(1)
C(F1)	-0.189(4)	0.236(4)	0.343(5)	9(1)
C(F2)	-0.202(7)	0.269(6)	0.454(9)	18(3)
C(F3)	-0.234(7)	0.378(6)	0.443(9)	18(3)
C(F4)	-0.339(5)	0.352(4)	0.363(6)	12(2)
C(F5)	-0.335(7)	0.304(7)	0.228(10)	20(3)
C(F6)	-0.298(6)	0.203(6)	0.255(8)	16(3)

Table 3. The anisotropic thermal parameters ($\times 10^4$) for silver and sulfur atoms. The temperature factor is expressed as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag(1)	78(2)	79(2)	116(12)	1(2)	20(2)	44(3)
Ag(2)	64(2)	81(2)	72(12)	-2(2)	28(2)	24(2)
Ag(3)	68(2)	72(2)	103(12)	1(1)	26(2)	33(2)
Ag(4)	103(3)	81(2)	126(12)	4(2)	58(3)	40(3)
Ag(5)	91(2)	79(2)	100(12)	2(2)	40(2)	30(3)
Ag(6)	67(2)	108(3)	102(12)	-18(2)	28(2)	-9(3)
S(A)	69(7)	60(6)	124(17)	5(5)	30(7)	18(7)
S(B)	76(8)	92(8)	114(18)	-12(6)	24(8)	40(8)
S(C)	65(7)	71(7)	97(16)	13(5)	27(7)	43(7)
S(D)	52(6)	41(6)	72(16)	8(4)	24(6)	8(6)
S(E)	41(5)	63(6)	73(15)	2(4)	16(6)	32(7)
S(F)	75(7)	78(7)	86(16)	9(6)	32(7)	43(7)

Lorentz and polarization effects but not for absorption or extinction.

Determination of the structure. The space group was assumed to be $P\bar{1}$. The position vectors r_i of the silver atoms were determined from the corresponding interatomic vectors $2r_i$ in the three-dimensional Patterson function. The vectors $2r_i$ were identified by systematic addition and subtraction of Patterson vectors using the relations: $(r_n + r_m) + (r_n - r_m) = 2r_n$ and $(r_n + r_m) - (r_n - r_m) = 2r_m$.

The silver atom coordinates were next refined by Fourier and least-squares calculations. Data up to $\sin \theta/\lambda = 0.35$ were included and the reliability index, $R = \sum |F_o| - |F_c| / \sum |F_o|$, became 0.17 after 3 cycles. The positions of the sulfur and carbon atoms were located from consecutive difference syntheses alternating with least-squares refinements. The electron densities of some of the carbon atoms were quite low, and the positions of C(B2)–C(B5) were roughly determined by geometrical considerations.

In the concluding least-squares refinement the expression $\sum w(|F_o| - |F_c|)^2$ was minimized using a full-matrix program.⁸ The weights, w , which in the previous computations had been unity, were now calculated from the formula suggested by Cruickshank $w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$ with $a = 20.0$, $c = 0.0057$, and $d = 0.00005$ as final values. Atomic scattering factors for silver and sulfur were taken from Hanson *et al.*⁹ and carbon from International Tables of X-Ray Crystallography, Vol. 3 (1962). Correction for dispersion was applied to silver. 18 very weak reflections, which lay outside the range $0.5 < |F_o|/|F_c| < 2.0$, were excluded. When the positional parameters and an individual isotropic temperature factor for each atom were refined together with an overall scale factor, R became 0.110. When anisotropic temperature factors for the silver and sulfur atoms were

introduced, R decreased to 0.084. The largest change in a silver or sulfur coordinate was 0.0014, when the anisotropic temperature factors were introduced. When the nineteen inter- and intra-layer scale factors and the atomic parameters were refined together, the value of R decreased to 0.080. The final values of the atomic parameters are presented in Tables 2 and 3. The observed and calculated structure factors can be obtained from the authors on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Notation. The silver atoms are denoted Ag(1)–Ag(6), and the ligands A–F. In each of the cyclohexane rings the carbon atoms are numbered 1 to 6. The carbon atom 1 is bonded to the sulfur atom. For example the carbon atom C(D1) is bonded to S(D) in the ligand D. Atoms related by a center of symmetry to those given in Table 2 are marked with a bar.

In the figures the silver atoms were denoted by the numbers 1 to 6 and the sulfur atoms by A–F.

General features. The metal atoms and ligands are linked together by Ag–S bonds to form unlimited polymer chains running parallel to the crystallographic c -axis. Fig. 1 gives an illustration of a part of a chain. The silver and sulfur atoms form the central core which is surrounded and shielded by the cyclohexyl groups of the ligands. The only contacts between atoms in different chains occur among the cyclohexyl groups and are of the van der

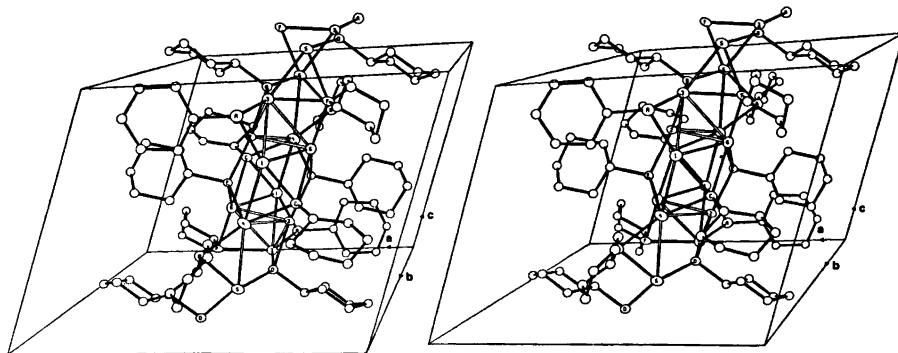


Fig. 1. A stereoscopic view of the unit cell. Silver atoms situated to a distance less than 3.3 Å from each other are connected by open lines. The silver-sulfur coordination ($\text{Ag}-\text{S} < 2.9 \text{ \AA}$) is marked by filled lines.

Waals type. The shortest interligand distances are given in Table 4.

The silver-sulfur arrangement. The framework of the silver and sulfur atoms can be seen in Fig. 1. The interatomic distances are given in Table 5. The silver atoms form two parallel chains, $-\text{Ag}(\bar{5})-\text{Ag}(\bar{4})-\text{Ag}(1)-\text{Ag}(3)-\text{Ag}(\bar{5})-$ and $-\text{Ag}(\bar{3})-\text{Ag}(\bar{1})-\text{Ag}(4)-\text{Ag}(5)-\text{Ag}(\bar{3})-$, which are related by a centre of symmetry and crosslinked through the atoms $\text{Ag}(2)$, $\text{Ag}(6)$, $\text{Ag}(\bar{2})$ and $\text{Ag}(\bar{6})$. The metal-metal distances range from 2.91 to 3.11 Å in the chains and from 3.03 to 3.29 Å in the cross links. These intermetallic distances are slightly longer than those in the metallic phase of silver (2.89 Å).¹⁰ Comparable Ag-Ag distances have been reported

in $[(\text{C}_3\text{H}_7)_2\text{NCS}_2\text{Ag}]_6$,³ $[(\text{C}_3\text{H}_7)_2\text{NCOSAg}]_6$,⁴ $\text{Ag}[\text{SC}(\text{NH}_2)_2]_2\text{Cl}$,¹¹ Ag_3AsS_3 ,¹² Ag_5SbS_4 ,¹³ and also in a number of other silver compounds.

Eight of the silver atoms of the unit cell have three-fold, almost planar coordination, while four of them have two-fold, nearly linear coordination. The structure accordingly can be described as a framework of coordination triangles and almost linear S-Ag-S segments. Fig. 2 shows the schematic representation of the triangles and segments which will be used in the following treatment. The coordination triangles are arranged in two groups, each comprising four triangles. The triangles share vertices in such a way that in each case a central parallelogram is formed. The centres of the parallelograms are also centres of sym-

Table 4. Interligand distances shorter than 4 Å. The coordinates of the second atom in each pair are related to those given in Table 2 (x, y, z) by the operations (a-j).

a:	x, y, z	f:	$1-x, -y, 1-z$
b:	$x, 1+y, z$	g:	$-x, 1-y, 1-z$
c:	$1+x, y, z$	h:	$1-x, 1-y, 1-z$
d:	$1-x, -y, -z$	i:	$-x, -1-y, -z$
e:	$-x, -y, 1-z$	j:	$-x, -1-y, 1-z$
C(A2)-C(B6)	e 3.80(18)	C(B5)-C(B5)	j 3.74
-C(D6)	a 3.87(6)	C(C2)-C(F2)	e 3.99(11)
-C(F3)	g 3.99(11)	C(C5)-C(D4)	f 3.88(9)
C(A4)-C(A4)	h 3.95(11)	-C(D5)	f 3.83(8)
C(A6)-C(B3)	b 3.99	C(D3)-C(D4)	f 3.88(7)
C(B2)-C(B3)	i 3.83	C(E4)-C(E4)	d 3.71(11)
-C(C2)	a 3.42	-C(F6)	c 3.94(10)
C(B3)-C(B3)	i 3.40		
-C(C2)	a 3.43		
-C(C3)	a 3.79		

Table 5. Interatomic distances (Å) with their estimated standard deviations in parentheses.

Ag(1)–Ag(3)	2.992(5)	Ag(5)–Ag(3)	2.911(5)
–Ag(4)	3.020(5)	–Ag(4)	3.106(5)
–Ag(6)	3.025(5)	–S(B)	2.64(1)
–S(A)	2.36(1)	–S(D)	2.58(1)
–S(C)	2.40(1)	–S(F)	2.60(1)
Ag(2)–Ag(3)	3.025(5)	Ag(6)–Ag(1)	3.025(5)
–Ag(4)	3.287(5)	–Ag(2)	3.154(4)
–Ag(6)	3.154(4)	–Ag(3)	3.032(5)
–S(D)	2.41(1)	–S(C)	2.87(1)
–S(E)	2.42(1)	–S(E)	2.44(1)
		–S(F)	2.43(1)
Ag(3)–Ag(1)	2.992(5)	S(A)–C(A1)	1.85(4)
–Ag(2)	3.025(5)	S(B)–C(B1)	1.90(6)
–Ag(5)	2.911(5)	S(C)–C(C1)	1.88(6)
–Ag(6)	3.032(5)	S(D)–C(D1)	1.83(4)
–S(A)	2.44(1)	S(E)–C(E1)	1.81(4)
–S(D)	2.57(1)	S(F)–C(F1)	1.86(6)
–S(F)	2.64(1)		
Ag(4)–Ag(1)	3.020(5)		
–Ag(2)	3.286(5)		
–Ag(5)	3.106(5)		
–S(B)	2.40(1)		
–S(C)	2.50(1)		
–S(E)	2.75(1)		

metry in the structure with the coordinates 0,0,0 and 0,0,1/2. There are striking similarities in shape between the groups. In both cases the obtuse angle of the parallelograms is 118° (117.5 and 117.7°). The sides and short diagonals of the two parallelograms are almost equal in length (3.75, 4.02, 4.04 and 3.77, 3.98, 4.01 Å). Thus the parallelograms resemble fractions of a layer of closed-packed sulfur atoms. Since the distances are only slightly longer than those commonly expected for sulfur contacts (3.7 Å), sterical restrictions in the packing of the sulfur atoms can be of importance for the formation of the parallelogram configurations. Similar restrictions probably are also reflected in the short silver-silver distances. The groups are

linked together by sharing the vertices B, \bar{B} , \bar{F} , and F which leads to the infinite arrangement illustrated in Fig. 3. The four linear S–Ag–S bridges have also been included in this figure.

The coordination. Distances and angles of coordination are given in Table 5 and Fig. 4. For the three-coordinated silver atoms the silver-sulphur arrangement is almost planar. The distance from a silver atom to the plane defined by the three sulfur atoms is 0.13 Å for Ag(3), 0.05 Å for Ag(4), 0.16 Å for Ag(5), and 0.20 Å for Ag(6). Therefore, the coordination figure may be described as a much flattened pyramid. This configuration is a common feature for three-coordinated silver and is present in the structure of $\text{Ag}_2\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$,³ $\text{AgSO}(\text{C}_2\text{H}_5)_2$,⁴ $\text{Ag}[\text{SC}(\text{NH}_2)_2]_2\text{Cl}$,¹¹ and Ag_3AsS_3 .¹² The two-fold silver coordination is almost linear, with the S–Ag–S angles equal to 167 and 169°, which means that the silver atom in each case is at a distance of 0.25 Å from the line joining the sulfur atoms. Similar deviations from linearity for two-fold silver coordination have been reported by Lindqvist¹⁴ for AgSCN (S–Ag–N = 165°) and by Strickler¹⁵ for $\text{Pt}[\text{S}-\text{C}_2\text{H}_4-\text{P}(\text{C}_2\text{H}_5)_2]_2\text{AgNO}_3$ (S–Ag–S = 171°).

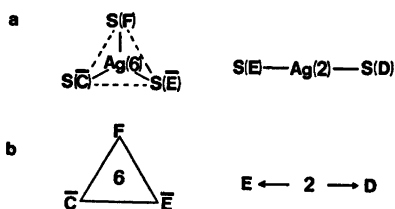


Fig. 2. Schematic representation (a) and notation (b) used for the silver-sulfur coordination.

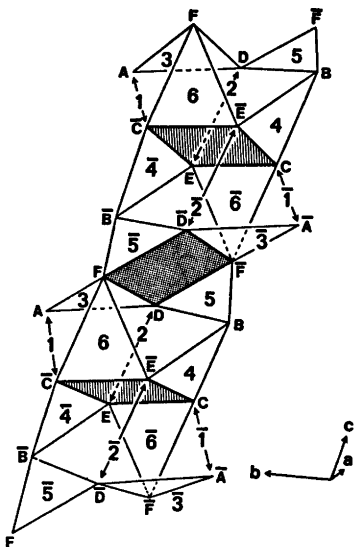


Fig. 3. A part of the infinite linkage of the coordination triangles and (linear) S-Ag-S segments.

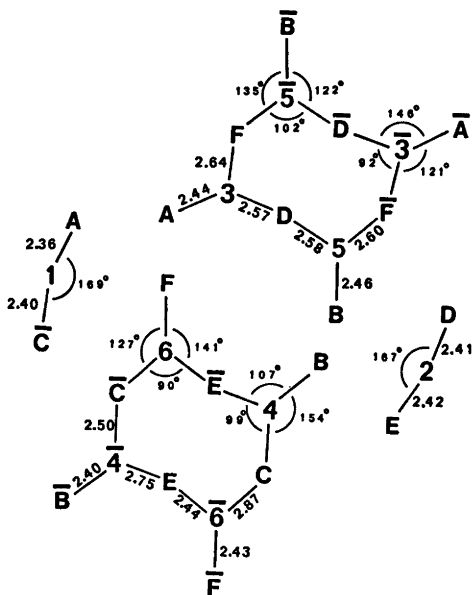


Fig. 4. Details of the coordination showing bond distances (Å) and bond angles (°).

The Ag-S distance is on the average 2.40 Å for two-fold and 2.56 Å for three-fold coordination of silver. The deviations from the average are small in the first group of distances,

and the mean value given above (2.40 Å) is equal to that reported for $\text{Pt}[\text{S}-\text{C}_2\text{H}_4-\text{P}(\text{C}_2\text{H}_5)_2]_2 \cdot \text{AgNO}_3$ ¹⁵ and AgCuS .¹⁶ For the three-coordinated silver atoms, more pronounced variations are observed in the distances which lie between 2.40 Å and 2.87 Å. Ag-Ag distances within this range are found in a number of compounds, for instance in Ag_5SbS_4 ³ and $\text{AgSCN} \cdot \text{P}(\text{C}_2\text{H}_5)_3$.¹⁷ The S-Ag distance is on the average 2.41 Å for two-fold and 2.55 Å for three-fold coordination of sulfur.

In the following list the Ag-S distances (in Å) are grouped according to the coordination numbers of the silver and sulfur atoms:

Ag 2, S 2
2.36
Ag 2, S 3
2.40, 2.41, 2.42 (av. 2.41)
Ag 3, S 2
2.40, 2.44, 2.46 (av. 2.43)
Ag 3, S 3
2.43, 2.44, 2.50, 2.57, 2.57, 2.58
2.60, 2.64, 2.75, 2.87 (av. 2.60)

One observes that all distances are short (≤ 2.46 Å) when one of the atoms involved is two-coordinated. In fact the shortest distance is found for the case where both atoms are two-coordinated. The longest distances, 2.75 and 2.87 Å, occur when the two atoms both are three-coordinated.

The ligands. The structural properties of cyclohexane and its derivatives are well-known from other investigations (see for instance Hassel and Viervoll¹⁸). Because of the presence of heavy atoms and since the number of structural parameters is high, the present compound is not very well suited for obtaining exact carbon positions. This is reflected in the high standard deviations of the atomic coordinates of the carbon atoms (Table 2). However, the positions are accurate enough to clearly show that the cyclohexyl rings are in the chair conformation (see also Fig. 1). One also observes that the carbon-sulfur bonds are oriented equatorially with respect to the cyclohexyl rings in all the ligands. The average value of the carbon-sulfur distance is 1.86 Å. Hassel and Viervoll¹⁸ obtained a value of 1.87 Å in cyclohexanethiol by electron diffraction investigations. Some recently reported



Fig. 5. Tubular arrangement of AX_3 -groups sharing vertices.

values^{19,20} for the single bonded carbon-sulfur distance range between 1.86 and 1.90 Å.

In a number of other silver (I) alkanethiolates studied by this group severe disorder effects have been observed. The high B -values in the temperature factors of the carbon atoms indicate that such effects are also of importance in the present compound.

In AgX compounds the coordination number of silver is 2 or 3 when X contains a bulky organic group. With two-fold coordination only, a structure can be realized from rings or unlimited chains for an AX compound. The latter alternative has been found in the structure of silver(I) 2,3-dimethylbutane-2-thiolate.²¹ AX_3 groups have been found to be joined to a tetrahedron in some copper(I) dithiocarbamates and to an octahedron in silver(I) dithiocarbamates. Arrangements based on $(A)X_3$ triangles connected by sharing edges can apparently not be realized for the silver(I) thiolates. If the $Ag-S$ distance is assumed to be 2.5 Å, one finds an $Ag-Ag$ distance 0.3 Å shorter than in metallic silver, even if the height of the silver atom above the S_3 -plane is as large as 0.5 Å. Arrangements of triangles sharing only corners yield longer metal-metal distances. Such arrangements can be constructed in a variety of ways. One example is given in Fig. 5. It contains the same group of four triangles as illustrated in Fig. 3. The fact that the present structure is not solely built from AgS_3 -groups sharing corners is probably caused by steric hindrances from the ligands.

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