The Crystal and Molecular Structure of the Silver(I)

Dipropyldithiocarbamate Hexamer

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The crystal structure of silver(I) dipropyldithiocarbamate, $(C_3H_7)_2NCS_2Ag$, has been determined from threedimensional X-ray data. The crystals are triclinic. Space group $P\bar{1}$. Unit cell parameters $a=11.374$ Å, $b=12.375$ Å, $c=12.997$ Å, $\alpha=96.10°$, $\beta=116.40°$, $\gamma=83.24°$. The structure consists of discrete hexameric molecules, $[(C_3H_7)_2NCS_2Ag]_6$, of which there is one per elementary cell. The metal atoms are situated in the central part of the $[(C_3H_7)_2NCS_2Ag]_6$ molecule and form a somewhat distorted octahedron with six comparatively short and six longer edges. The short edges correspond to metal-metal distances comparable to or somewhat longer than those in the metallic phase of silver. The long edges form two centrosymmetrically related triangles in the silver octahedron. Outside each of the other six faces of the octahedron one dithiocarbamate ligand is situated, linked to the silver atoms of the face by silver-sulphur coordination. One of the sulphur atoms is linked to one and the other to two silver atoms. The silver coordination is threefold but not planar, the metal atoms being situated "inside" the plane of the coordinating sulphur atoms. The dithiocarbamate ligands bear close resemblance to those studied in other dithiocarbamates.

The geometrical dependences between the distances and angles in the structure are discussed with the aid of a relation formulated by Hesse and it is found that the short metal-metal distances very well can be due to the metal-ligand linkage in the structure. The linkage in some of the simplest polymers of AX type is surveyed.

Compounds of the composition AX, where A and X, respectively, denote metal and ligand *atoms*, generally form high polymers in the solid state. Their crystal structures are usually very simple with regular coordination of the A and X atoms. Sodium chloride, caesium chloride, zinc blende, wurtzite, and nickel arsenide represent common and very wellknown structure types.

The situation is more complicated, however, when the ligand X is a *molecule*, which is large as compared with the metal atom A, and which is only accessible for coordination in a very unsymmetric way. Compounds of this type are found among univalent metal derivatives ("salts") of various organic acids. Their crystal structures are built of units, A and X, which differ exceed-

ingly in size and shape and requirements of coordination. The requirements of the units will often contradict each other and the arrangements, which can be formed will then represent compromises. Under these circumstances the metal atoms can show unusual coordination properties.

Several features of great interest can be found in structures of this type. Due to the space requirements and screening effects of the ligand molecules there will be a number of restrictions for the formation of networks by $A-X$-linkage. Unlimited three-dimensional $A-X$-networks are thus very unlikely. On the other hand the occurrence of isolated monomers, consisting of one metal atom and one ligand molecule, would be improbable because of the extremely unfavourable coordination conditions, which would then appear. Accordingly the arrangements which can be expected for these compounds can roughly be divided into the following types:

a) structures comprising two-dimensional $A-X$-networks;
b) chain structures;
c) arrangements built of isolated low polymers $(AX)_n$.

Representatives of all these types have been found by the research group to which the present authors belong. The group is currently engaged in crystal structure studies of dithiocarbamates, monothiocarbamates, and thiolates of univalent metals. Some of the structures have been described and discussed by Hesse.[1-3] The majority of the compounds hitherto examined occur as low polymers in the solid state, but there are also high polymers, occurring as chain and layer structures. Examples of high polymers are thallium(I) dipropyldithiocarbamate [4] and caesium(I) dibutyldithiocarbamate.[5] The low polymers, the structures of which have been determined, can be written $(AX)_2$, $(AX)_4$, and $(AX)_6$. Examples are $[(C_3H_7)_2NCS_2Au]_2$,[2] $[(C_2H_5)_2NCS_2Cu]_4$,[3] $[(C_2H_5)_2NCS_2Ag]_6$.[2]

Dithiocarbamates, monothiocarbamates, and thiolates of univalent metals usually form low polymers in solutions of inert organic solvents as has been shown by Åkerström.[6] The main polymers reported by him are dimers, tetramers, hexamers, octamers, and dodecamers. Among the compounds which form hexamers in solution are silver(I) dipropyldithiocarbamate, silver(I) dipropylmonothiocarbamate,[7] and copper(I) dipropylmonothiocarbamate.[8] All of them also occur as hexamers in the solid state. Their crystal structures have been determined by the present research group and will now be published. In this paper the molecular and crystal structure of the silver(I) dipropyldithiocarbamate hexamer, $[(C_3H_7)_2NCS_2Ag]_6$, is presented.

EXPERIMENTAL

Crystals of silver(I) dipropyldithiocarbamate were kindly provided by Dr. S. Åkerström,[9] who had prepared the compound according to his published method. The crystals were obtained from benzene and light petroleum ether as yellow rods. Their density was measured by the flotation method using an aqueous solution of K_2HgI_4. The cell parameters were determined from a powder photograph recorded in a Guinier-Hägg focussing camera using $CrK\alpha_1$ radiation ($\lambda = 2.2896$ Å) with elementary silicon ($a = 5.4305$ Å) [10] as a calibration standard.

For the single crystal work CuKα radiation was used. The X-ray reflexions were recorded on equi-inclination Weissenberg photographs with the use of multiple-film technique (five films). The relative intensities were estimated visually, the intensities being compared with a calibrated scale. Corrections were applied for absorption and for the Lorentz and polarisation effects. 1267 independent reflexions of non-zero intensity were used for the structure determination. The main intensity data were obtained from a crystal with the dimensions $0.07 \times 0.05 \times 0.23$ mm, the needle axis corresponding to [001]. Eleven layers ($0 \leq l \leq 10$) were collected with the crystal rotating about this axis. Interlayer scale factors were calculated using data obtained from another crystal with the dimensions $0.05 \times 0.03 \times 0.08$ mm, the *longest* edge corresponding to [001]. This crystal was rotated about the a-axis and four layers with $0 \leq h \leq 3$ were recorded.

UNIT CELL AND SYMMETRY

Formula unit: $(C_3H_7)_2NCS_2Ag$
Crystal system: triclinic
Space group: $P\bar{1}$
Unit cell parameters:

$a = 11.374 \pm 0.005$ Å, $b = 12.375 \pm 0.005$ Å, $c = 12.997 \pm 0.005$ Å.
$\alpha = 96.10° \pm 0.02$, $\beta = 116.40° \pm 0.02$, $\gamma = 83.24° \pm 0.04$.

Volume of unit cell: 1624 Å³
Density (measured): 1.736 gcm⁻³
Number of formula units per unit cell: 6
Density (calculated): 1.743 gcm⁻³

DETERMINATION OF THE ATOMIC POSITIONS

Approximate positions of the silver and sulphur atoms were derived from the three-dimensional Patterson function. The coordinates of these atoms were adjusted by three-dimensional Fourier calculations using back-shift technique. The nitrogen and carbon atoms were located from successive three-dimensional difference syntheses. It was, however, not possible to locate the hydrogen atoms by these methods. For the structure factor calculations and the Fourier summations the programmes STRIX/PROFFS[11] and DRF (written by A. Zalkin, Berkeley, Calif., U.S.A. and modified by R. Liminga and J. O. Lundgren, Uppsala) were used. The coordinates and isotropic temperature factors of all but the hydrogen atoms were refined by the method of least squares. The first series of these calculations was performed on the electronic computer FACIT EDB employing the programme SFLS,[12] which uses a block-diagonal approximation. In a final series of refinement the calculations were carried out on a CD 3600 computer with the full-matrix programme LALS.[13] In the expression $\sum \omega(|F_o| - |F_c|)^2$, which was minimized, the weights, ω, were calculated according to the equation, suggested by Cruickshank *et al.*,[14] $\omega = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$. The constants used in the final cycles were $a = 21.3$, $c = 0.00845$, and $d = 0.00009$. The final weight analysis is given in Table 1. Atomic scattering factors for the elements were obtained from the following sources: silver, Thomas and Umeda,[15] sulphur,

Table 1. Final weight analysis.

Interval $\sin\theta$	$\overline{\omega\,\Delta^2}$ normalized	Number of reflexions	Interval F_0	$\overline{\omega\,\Delta^2}$ normalized	Number of reflexions
0.00 — 0.43	1.43	464	0 — 24	1.00	123
0.43 — 0.54	0.95	356	24 — 29	1.18	125
0.54 — 0.62	1.30	221	29 — 35	0.80	126
0.62 — 0.68	1.28	115	35 — 40	0.89	125
0.68 — 0.73	1.29	54	40 — 45	1.06	126
0.73 — 0.78	1.20	25	45 — 52	1.14	125
0.78 — 0.82	0.85	10	52 — 61	0.80	125
0.82 — 0.86	0.74	6	61 — 73	0.97	127
0.86 — 0.89	0.71	2	73 — 96	0.95	126
0.89 — 0.93	0.24	2	96 — 234	1.20	127

Dawson,[16] nitrogen and carbon, Hoerni and Ibers.[17] Dispersion corrections for silver and sulphur were introduced into the calculations.[18]

The least squares calculations were continued until the shifts of the parameters were less than one tenth of the estimated standard deviations. At this stage of the refinement the discrepancy index, R, was 0.101. The atomic coordinates and isotropic temperature factors obtained from the last cycle can all be found in Table 2. For the atoms marked by an asterisk in this table the least squares values are, however, given in parentheses. The coordinates of these atoms presented without parentheses are obtained from geometrical calculations combined with considerations of the electron density distribution. The least squares values were regarded as less accurate because they gave

Table 2. Atomic parameters. The parameters of all atoms, with the exception of those marked by an asterisk, are taken from the final least squares refinement. The coordinates of the atoms marked by an asterisk are determined from geometrical considerations and the electron density distribution. The least squares parameters of these atoms are given in parentheses. The coordinates of atoms with the notations $\bar{\mathrm{I}}$, $\bar{\mathrm{II}}$, and $\bar{\mathrm{III}}$ can be obtained from those in the table by reversing the signs of the coordinates.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B Å^2	$\sigma(B)$ Å^2
Metal atoms								
Ag_I	0.1156	0.0004	0.1319	0.0003	−0.0555	0.0003	5.69	0.10
Ag_{II}	0.1602	0.0004	−0.1417	0.0003	0.1030	0.0003	6.22	0.11
Ag_{III}	−0.0156	0.0004	0.0829	0.0003	0.1609	0.0003	5.89	0.11
Dithiocarbamate ligand I								
S_{IA}	0.0480	0.0012	0.1932	0.0010	−0.2464	0.0012	5.9	0.3
S_{IB}	−0.1661	0.0011	0.0469	0.0009	−0.2824	0.0011	5.2	0.3
C_I	−0.077	0.004	0.125	0.004	−0.326	0.004	5.7	1.1
N_I	−0.153	0.003	0.145	0.003	−0.445	0.003	4.7	0.8
C_{IA1}	−0.099	0.004	0.214	0.003	−0.497	0.004	5.7	1.1
C_{IA2}	0.012	0.005	0.148	0.004	−0.526	0.005	8.7	1.4
C_{IA3}	0.084	0.005	0.220	0.004	−0.570	0.005	9.0	1.5
C_{IB1}	−0.279	0.005	0.097	0.004	−0.525	0.004	7.3	1.3
C_{IB2}	−0.397	0.005	0.180	0.004	−0.533	0.005	7.8	1.4
C_{IB3}	−0.523	0.006	0.128	0.005	−0.613	0.005	9.5	1.6

Dithiocarbamate ligand II

S_{IIA}	0.1634	0.0013	−0.3314	0.0011	0.0301	0.0013	7.0	0.3
S_{IIB}	−0.0985	0.0012	−0.2245	0.0010	−0.1219	0.0011	5.6	0.3
C_{II}	0.017	0.004	−0.331	0.004	−0.088	0.004	6.2	1.1
N_{II}	−0.015	0.004	−0.424	0.004	−0.163	0.004	9.1	1.2
C_{IIA1}	0.063	0.006	−0.530	0.005	−0.136	0.005	10.6	1.6
C_{IIA2}	0.205	0.009	−0.533	0.007	−0.137	0.008	16.0	2.8
C_{IIA3}	0.160	0.009	−0.510	0.007	−0.273	0.008	13.1	2.7
C_{IIB1}	−0.132	0.005	−0.435	0.004	−0.277	0.005	7.1	1.3
C_{IIB2} *	−0.230		−0.501		−0.262		15	
	(−0.216	0.009	−0.480	0.007	−0.268	0.008	14.6	2.8)
C_{IIB3}	−0.344	0.009	−0.508	0.007	−0.379	0.008	19.4	3.4

Dithiocarbamate ligand III

S_{IIIA}	−0.2267	0.0015	0.1307	0.0012	0.1740	0.0014	7.6	0.4
S_{IIIB}	−0.2853	0.0012	0.0132	0.0010	−0.0534	0.0012	5.7	0.3
C_{III}	−0.332	0.004	0.113	0.003	0.031	0.004	4.3	0.9
N_{III}	−0.459	0.005	0.143	0.004	−0.010	0.004	8.6	1.2
C_{IIIA1}	−0.508	0.006	0.221	0.005	0.068	0.005	9.8	1.6
C_{IIIA2}	−0.471	0.006	0.327	0.005	0.069	0.006	10.6	1.7
C_{IIIA3}	−0.521	0.009	0.389	0.007	0.155	0.008	15.9	2.7
C_{IIIB1}	−0.554	0.006	0.119	0.005	−0.135	0.005	9.6	1.6
C_{IIIB2}*	−0.535		0.202		−0.202		15	
	(−0.539	0.008	0.213	0.007	−0.220	0.008	15.0	2.5)
C_{IIIB3}	−0.634	0.009	0.195	0.007	−0.321	0.008	16.0	2.6

interatomic distances and angles in the propyl chains, which were considered to deviate too much from expected values (see Table 5). The discrepancy index, R, changed to 0.103 after this operation. Interatomic distances and angles are given in Tables 3—6. Values given in parentheses correspond to coordinates given in parentheses in Table 2. For the notation of the atoms, see the following section.

Table 3. Metal-metal distances.

(Distances in Å)

$Ag_I − Ag_{\overline{II}}$	2.905 ± 0.005	$Ag_I − Ag_{II}$	4.014 ± 0.005
$− Ag_{\overline{III}}$	2.965 ± 0.005	$Ag_{I} − Ag_{\overline{III}}$	3.199 ± 0.006
$− Ag_{nI}$	3.849 ± 0.005	$− Ag_{III}$	3.446 ± 0.005

Table 4. Distances and angles of coordination.

a. *Distances*

Atoms	Distance (Å)
$Ag_I − S_{IA}$	2.427 ± 0.014
$− S_{\overline{IIIB}}$	2.500 ± 0.013
$− S_{\overline{IIB}}$	2.540 ± 0.013
$Ag_{II} − S_{IIA}$	2.439 ± 0.013
$− S_{\overline{IB}}$	2.473 ± 0.013
$− S_{\overline{IIIB}}$	2.556 ± 0.013

Table 4. Continued.

$$Ag_{III}-S_{IIIA} \qquad 2.480 \pm 0.016$$
$$-S_{\bar{I}B} \qquad 2.490 \pm 0.012$$
$$-S_{\bar{II}B} \qquad 2.514 \pm 0.013$$

b. *Angles*

Atoms	Angle (°)	Atoms	Angle (°)
$S_{IA}-Ag_I-S_{\bar{II}B}$	132.1 ± 0.4	$C_I-S_{IA}-Ag_I$	103.5 ± 1.8
$S_{IA}-Ag_I-S_{\bar{III}B}$	131.2 ± 0.5	$C_I-S_{IB}-Ag_{\bar{II}}$	105.7 ± 1.6
$S_{\bar{II}B}-Ag_I-S_{\bar{III}B}$	94.1 ± 0.4	$C_I-S_{IB}-Ag_{\bar{III}}$	99.9 ± 1.5
		$Ag_{\bar{II}}-S_{IB}-Ag_{\bar{III}}$	87.9 ± 0.4
$S_{IIA}-Ag_{II}-S_{\bar{I}B}$	135.3 ± 0.5		
$S_{IIA}-Ag_{II}-S_{\bar{III}B}$	117.2 ± 0.5	$C_{II}-S_{IIA}-Ag_{II}$	100.9 ± 1.6
$S_{\bar{I}B}-Ag_{II}-S_{\bar{III}B}$	100.0 ± 0.4	$C_{II}-S_{IIB}-Ag_{\bar{I}}$	111.7 ± 1.7
		$C_{II}-S_{IIB}-Ag_{\bar{III}}$	101.8 ± 1.6
$S_{IIIA}-Ag_{III}-S_{\bar{I}B}$	125.5 ± 0.5	$Ag_{\bar{I}}-S_{IIB}-Ag_{\bar{III}}$	99.2 ± 0.4
$S_{IIIA}-Ag_{III}-S_{\bar{II}B}$	121.0 ± 0.5		
$S_{\bar{I}B}-Ag_{III}-S_{\bar{II}B}$	104.6 ± 0.4	$C_{III}-S_{IIIA}-Ag_{III}$	98.7 ± 1.5
		$C_{III}-S_{IIIB}-Ag_{\bar{I}}$	115.3 ± 1.5
		$C_{III}-S_{IIIB}-Ag_{\bar{II}}$	94.5 ± 1.3
		$Ag_{\bar{I}}-S_{IIIB}-Ag_{\bar{II}}$	105.1 ± 0.5

Table 5. Distances and angles in the dithiocarbamate ligands. The values given in parentheses represent distances or angles based on cordinates given in parentheses in Table 2.

a. *Distances in Å.*

Atoms	Ligands	I	II	III	Average
$S_A \cdots S_B$		3.045 ± 0.017	2.987 ± 0.019	2.976 ± 0.021	3.00
$C-S_A$		1.62 ± 0.05	1.70 ± 0.05	1.71 ± 0.04	1.68
$C-S_B$		1.77 ± 0.05	1.69 ± 0.05	1.76 ± 0.04	1.74
$C-N$		1.43 ± 0.06	1.40 ± 0.07	1.32 ± 0.06	1.38
$N-C_{A1}$		1.48 ± 0.06	1.47 ± 0.07	1.56 ± 0.08	1.50
$N-C_{B1}$		1.48 ± 0.06	1.49 ± 0.07	1.52 ± 0.08	1.50
$C_{A1}-C_{A2}$		1.58 ± 0.07	1.61 ± 0.11	1.43 ± 0.09	1.54
$C_{A2}-C_{A3}$		1.57 ± 0.08	1.65 ± 0.13	1.57 ± 0.11	1.60
$C_{B1}-C_{B2}$		1.56 ± 0.08	1.55	1.50	
			(1.21 ± 0.10)	(1.74 ± 0.11)	
$C_{B2}-C_{B3}$		1.52 ± 0.08	1.50	1.46	
			(1.57 ± 0.13)	(1.30 ± 0.13)	

b. *Angles in degrees.*

Atoms	Ligands	I	II	III	Average
S_A-C-S_B		128.1 ± 3.0	124.2 ± 2.8	118.1 ± 2.3	123.5
S_A-C-N		120.9 ± 3.3	119.2 ± 3.4	122.5 ± 3.5	120.9
S_B-C-N		109.0 ± 3.0	116.7 ± 3.4	116.0 ± 3.3	113.9
$C-N-C_{A1}$		117.3 ± 3.3	123.4 ± 4.4	118.0 ± 4.4	119.6
$C-N-C_{B1}$		126.6 ± 3.5	126.5 ± 4.2	122.3 ± 4.5	125.1
$C_{A1}-N-C_{B1}$		116.1 ± 3.5	110.1 ± 4.2	119.0 ± 4.4	115.0
$N-C_{A1}-C_{A2}$		112.0 ± 3.5	114.8 ± 5.1	107.4 ± 4.9	109.7
$C_{A1}-C_{A2}-C_{A3}$		114.4 ± 4.1	101.0 ± 6.2	99.5 ± 5.5	104.6
$N-C_{B1}-C_{B2}$		109.5 ± 3.8	107.6	106.0	
			(110.2 ± 5.9)	(109.3 ± 4.8)	
$C_{B1}-C_{B2}-C_{B3}$		108.0 ± 4.3	104.5	110.1	
			(119.5 ± 7.6)	(104.8 ± 6.8)	

Table 6. Interligand distances shorter than 4.0 Å. The coordinates of the atoms with the additional notations (a)−(i) are related to those given in Table 2 (coordinates x,y,z) as follows:

$-x$	$1-y$	$-z$	(a)
$-x$	$-y$	$1-z$	(b)
$-(1+x)$	$-y$	$-z$	(c)
$-(1+x)$	$-y$	$1-z$	(d)
$-(1+x)$	$1-y$	$1-z$	(e)
x	y	$z-1$	(f)
x	$y-1$	z	(g)
$1+x$	y	z	(h)
$1+x$	$1+y$	z	(i)

Atoms		Distance (Å)	Atoms		Distance (Å)
S_{IB} −S_{IIB}		3.96	N_I −C_{IA2}	(b)	3.84
S_{IB} −S_{IIIB}		3.85	N_{III} −N_{III}	(c)	3.83
S_{IIB} −S_{IIIB}		3.69	N_{III} −C_{IIIB1}	(c)	3.89
S_{IA} −C_{IIA1}	(g)	3.57	C_{IA2} −C_{IA2}	(b)	3.87
S_{IA} −C_{IIA2}	(g)	3.81	C_{IA2} −C_{IB1}	(b)	3.92
S_{IB} −C_{IA3}	(b)	3.87	C_{IA2} −C_{IIIB3}	(h)	3.79
S_{IB} −C_{IB3}	(d)	4.00	C_{IA3} −C_{IIB1}	(b)	3.71
S_{IIA} −$C_{\overline{III}}$		3.83	C_{IA3} −C_{IIIB3}	(h)	3.41
S_{IIA} −C_{IIB2}	(a)	3.59	C_{IB1} −C_{IIIB3}	(d)	3.95
S_{IIIA}−C_{IA1}	(f)	3.92	C_{IIA2}−C_{IIIA2}	(i)	3.92
S_{IIIA}−C_{IA2}	(f)	3.63	C_{IIA2}−$C_{\overline{III}A2}$		3.98
S_{IIIA}−C_{IA3}	(f)	3.80	C_{IIA2}−C_{IIIA3}	(i)	3.86
S_{IIIB}−C_{IIIA1}	(c)	3.88	C_{IIB2}−C_{IIIA3}	(d)	3.80
C_I −C_{IA2}	(f)	3.87	C_{IIB3}−C_{IIB3}	(e)	3.54
C_{III} −C_{IIB1}	(c)	3.88			

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Notations. The silver atoms and dithiocarbamate ligands for which the atomic coordinates are given in Table 2 are denoted by I, II, and III. The metal atoms and ligands which are related to these by a centre of symmetry in the origin are designated $\bar{I}$, $\overline{II}$, and $\overline{III}$. The individual atoms of the dithio-
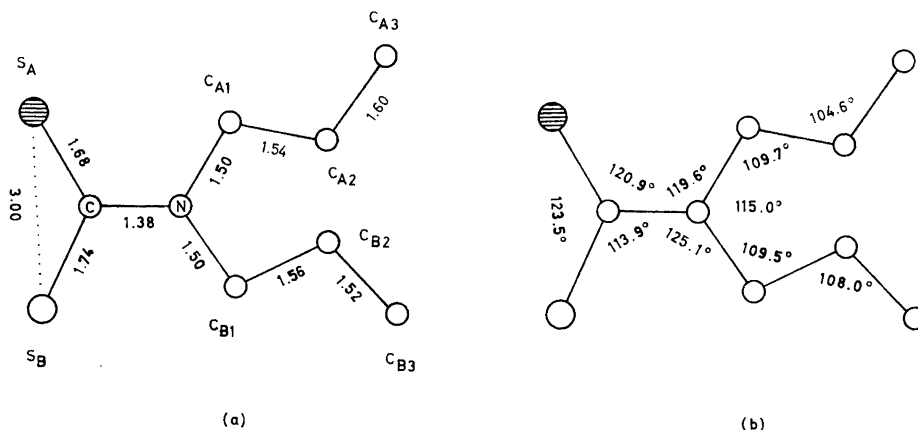

Fig. 1. The dithiocarbamate ligand. Notation of the atoms. Average distances (a) and angles (b) according to Table 5.

carbamate ligands are given additional notations according to Fig. 1. The propyl chains A and B correspond to the sulphur atoms S_A and S_B, respectively, as is shown in the figure. As an example $C_{\overline{III}A1}$ means the carbon atom C_{A1} of the dithiocarbamate ligand $\overline{III}$. For further notations see Table 6.

Molecular arrangement. The crystal structure of silver(I) dipropyldithiocarbamate is built from discrete $[(C_3H_7)_2NCS_2Ag]_6$ molecules. There is one
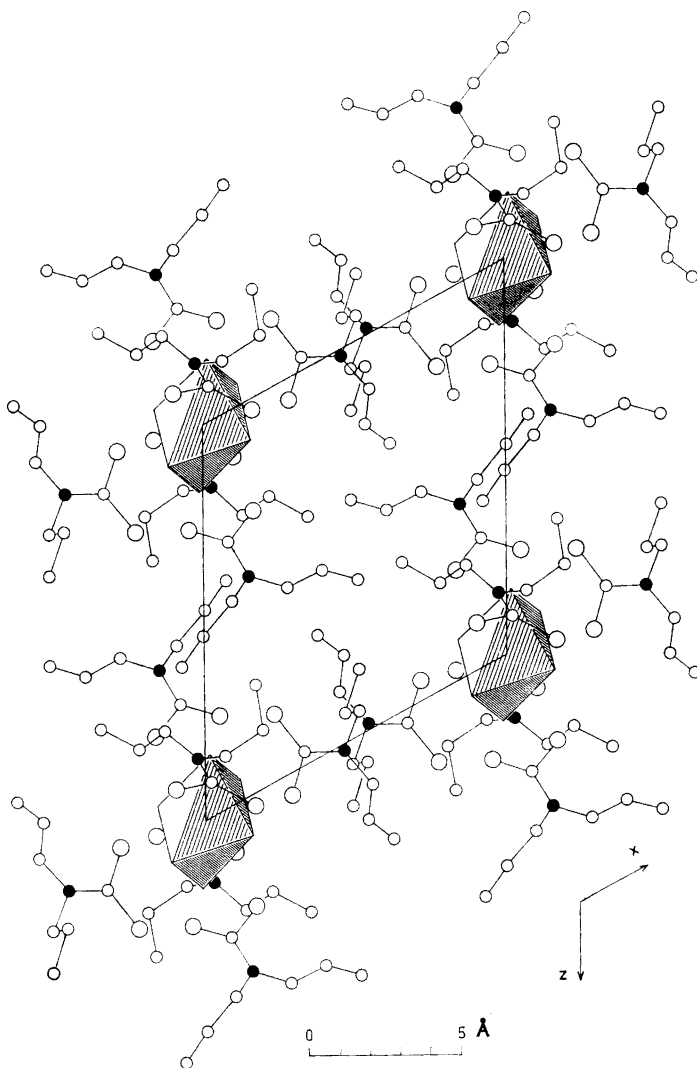

Fig. 2. The crystal structure of silver(I) dipropyldithiocarbamate. [010]-projection. The silver atoms are situated at the apices of the octahedra. The equatorial faces are shaded as in Figs. 3 and 4.

hexamer of this kind per elementary cell, with its molecular centre situated at the origin according to the present choice of axes. The packing of the molecules is shown in Fig. 2. In each of the hexameric molecules the metal atoms and the ligands are linked together by Ag—S bonds as will be described in more detail later. There are no bonds of this kind between different hexamers, the intermolecular Ag—S distances exceeding 6 Å. The central active part of a molecule, comprising silver and sulphur atoms, is accordingly shielded by the surrounding inert alkyl groups and the forces acting between different hexamers are of van der Waals' type. Intermolecular distances shorter than 4.0 Å are given in Table 6.
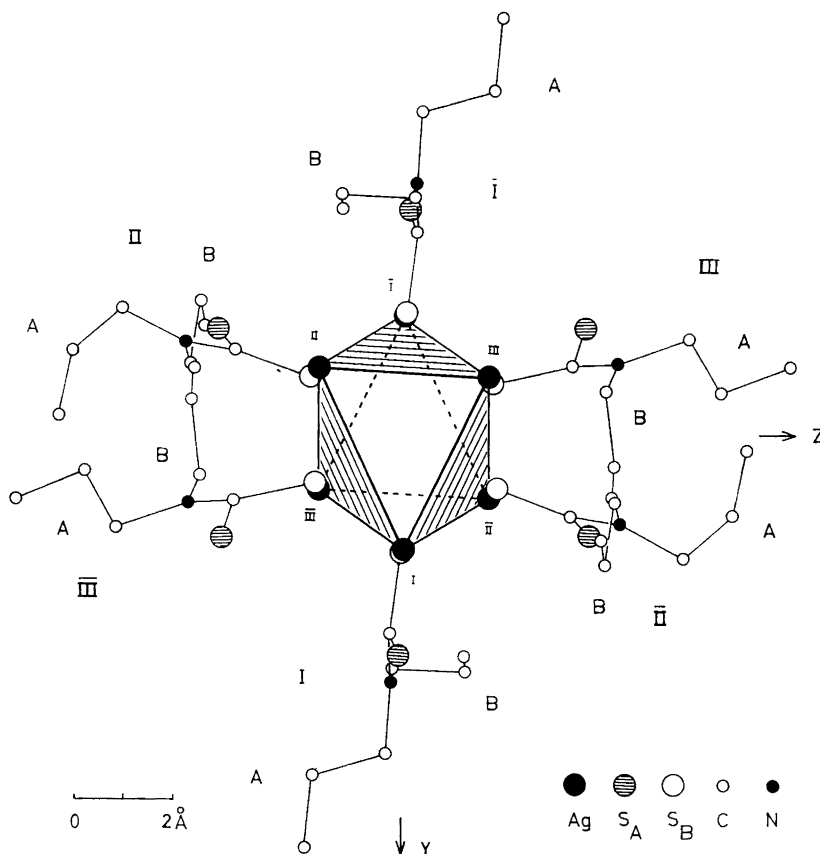
Fig. 3. The $[(C_3H_7)_2NCS_2Ag]_6$-molecule. Orthogonal projection in a direction perpendicular to the $Ag_IAg_{II}Ag_{III}$ plane. The ligands are situated outside the equatorial faces (shaded in the figure) of the central silver octahedron. The coordinate system XYZ has its origin at the centre of the molecule. The Y- and Z-axes are parallel to the plane of the projection while the X-axis is perpendicular to it. The coordinates of the atoms in this system are given in Table 7 in Ångström units, and the deviations of the atoms from the YZ-plane can accordingly be obtained from the X-coordinates in this table.

THE HEXAMER

The $[(C_3H_7)_2NCS_2Ag]_6$ molecule is centrosymmetric. The molecule comprises atoms with the general notations I, II, III, and atoms, which are related to these by a centre of symmetry and have the notations $\bar{I}$, $\bar{II}$, $\bar{III}$. A diagram of a hexamer is given in Fig. 3, which is an orthogonal projection in a direction perpendicular to the plane of the atoms Ag_I, Ag_{II}, and Ag_{III}. Table 7 is a good complement to Fig. 3 for the description of the structure. In this table

Table 7. Atomic coordinates in Ångström units in the orthonormalized coordinate system, XYZ (*cf.* Fig. 3). The coordinates of atoms with the notations $\bar{I}$, $\bar{II}$, and $\bar{III}$ can be obtained from those in the table by reversing the signs of the coordinates.

	X	Y	Z
Metal atoms			
Ag_I	1.05	2.33	0.00
Ag_{II}	1.05	-1.30	-1.73
Ag_{III}	1.05	-1.12	1.71
Dithiocarbamate ligand I			
S_{IA}	-0.14	4.44	-0.09
S_{IB}	-2.39	2.39	-0.04
C_I	-1.68	4.00	-0.25
N_I	-2.73	4.97	-0.22
C_{IA1}	-2.34	6.39	-0.32
C_{IA2}	-1.99	6.82	-1.80
C_{IA3}	-1.43	8.28	-1.94
C_{IB1}	-4.19	4.70	-0.20
C_{IB2}	-4.70	4.76	1.27
C_{IB3}	-6.19	4.46	1.26
Dithiocarbamate ligand II			
S_{IIA}	-0.08	-2.05	-3.76
S_{IIB}	-2.21	-1.11	-1.89
C_{II}	-1.69	-1.65	-3.40
N_{II}	-2.67	-1.80	-4.39
C_{IIA1}	-2.42	-2.48	-5.67
C_{IIA2}	-1.58	-1.62	-6.67
C_{IIA3}	-2.37	-0.32	-6.95
C_{IIB1}	-4.09	-1.37	-4.30
C_{IIB2}	-4.96	-2.63	-4.10
C_{IIB3}	-6.36	-2.12	-4.03
Dithiocarbamate ligand III			
S_{IIIA}	-0.14	-2.10	3.66
S_{IIIB}	-2.18	-0.99	1.79
C_{III}	-1.66	-1.35	3.43
N_{III}	-2.62	-1.41	4.34
C_{IIIA1}	-2.24	-1.89	5.77
C_{IIIA2}	-1.55	-0.82	6.42
C_{IIIA3}	-1.17	-1.34	7.82
C_{IIIB1}	-4.00	-0.84	4.10
C_{IIIB2}	-3.88	0.65	4.28
C_{IIIB3}	-5.19	1.27	4.23

the atomic coordinates are given in Ångström units in an orthonormalized coordinate system, XYZ. The directions of the axes in this system are indicated in the figure. The Y- and Z-axes are parallel to the plane of the projection. The X-axis is perpendicular to this plane. The origin of the coordinate system is situated at the centre of the molecule.

As is seen from Table 7 the silver and sulphur atoms in a hexamer are situated close to five levels parallel to the YZ-plane. The X-coordinates of these levels are: 0 Å (S_A); ±1.05 Å (Ag); ±2.25 Å (S_B). The ligands I, II, and III are inclined downwards and the ligands $\bar{I}$, $\bar{II}$, and $\bar{III}$ upwards in Fig. 3. The structure of the hexamer can be regarded as a deformation of an arrangement with the symmetry $\bar{3}$ and can accordingly be described as having the pseudosymmetry $\bar{3}$. It is reasonable to expect that in solution the molecule, or at least the central part of it, has the symmetry $\bar{3}$, and that the deformation observed in the crystal structure is due to packing effects.

The metal-metal distances are given in Table 3. The metal atoms in the central part of the molecule form a somewhat distorted octahedron with six comparatively short and six longer edges. The short edges correspond to metal-metal distances comparable to or somewhat longer than those in the metallic phase of silver (2.89 Å).[19] The long edges form two centrosymmetrically related triangles, which are called the "polar faces" of the silver octahedron. These "polar" triangles, $Ag_IAg_{II}Ag_{III}$ and $Ag_{\bar{I}}Ag_{\bar{II}}Ag_{\bar{III}}$, are parallel to the plane of the projection in Fig. 3. In each of the other six faces of the octahedron, the "equatorial faces", there are two short edges and one long. The ligands are situated outside these "equatorial" faces.
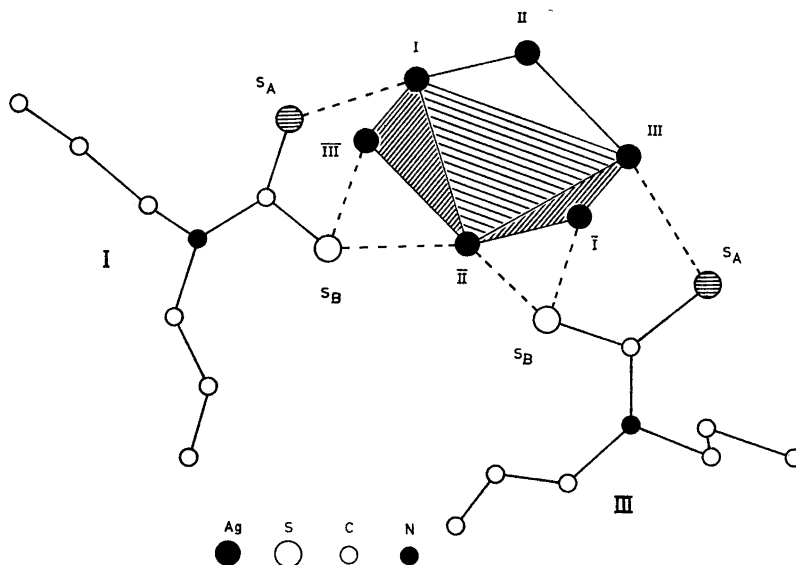

Fig. 4. Detail of a hexamer showing the linkage of two ligands to the silver octahedron. Equatorial faces are shaded. [010]-projection (*cf.* Fig. 2).

The polar triangles are connected to each other by the short edges of the octahedron. The average distance between silver neighbours belonging to different polar triangles is 3.0 Å, while the average distance between silver atoms belonging to the same polar triangle is 3.8 Å. Intermetallic distances comparable with the short metal-metal distances in silver(I) dipropyldithio-carbamate also occur in some other compounds, for instance silver fulminate,[20] AgCNO (2.82 and 2.93 Å for the rhombohedral and the orthorhombic forms, respectively), xanthoconite,[21] Ag_3AsS_3 (2.95—3.09 Å), and phenylethynyl-(trimethylphosphine)silver(I),[22] $C_6H_5C \equiv CAgP(CH_3)_3$ (3.03 Å).

Coordination. The general principle of the linkage between the metal atoms A and the ligands X is shown in Fig. 6c. Each metal atom is linked to three ligands and each ligand to three metal atoms. The distances and angles of coordination are presented in Table 4. Detailed pictures of the coordination are given in Figs. 4 and 5.

The ligands are attached to the metal atoms of the equatorial triangles in the manner shown in Fig. 4. One of the sulphur atom, S_A, of each ligand coordinates one silver atom, while the other sulphur atoms, S_B, coordinate two silver atoms. These last mentioned silver atoms both belong to the same polar triangle of the octahedron. The three silver atoms of a polar triangle
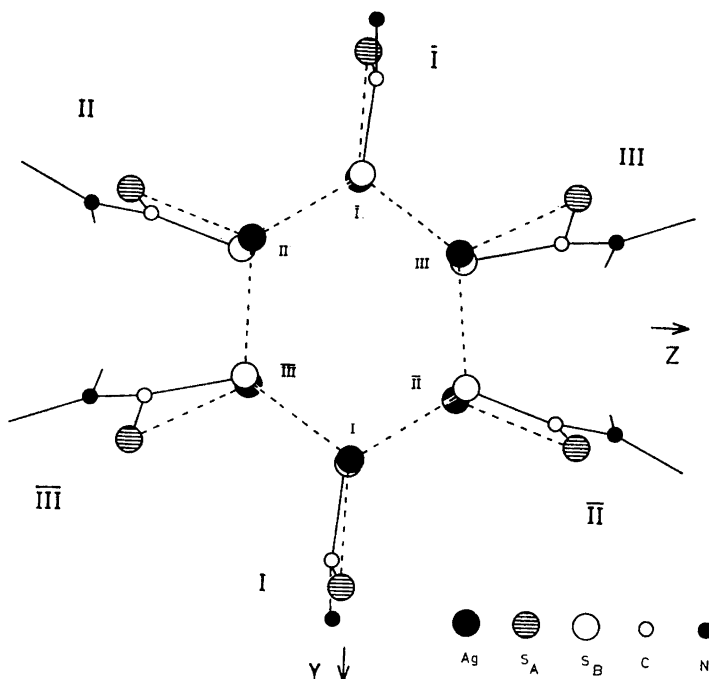

Fig. 5. The central part of a hexamer showing the metal coordination. To get a more clear picture the lines indicating the coordination between the silver atoms $Ag_{\bar{I}}$, $Ag_{\bar{II}}$, $Ag_{\bar{III}}$, and the sulphur atoms S_B have been omitted.

(*e.g.* Ag_I, Ag_{II}, Ag_{III}) are thus held together by $Ag-S_B-Ag$ bridges as is shown in Fig. 5. The silver atom coordinated by the sulphur atom S_A of a certain ligand does not belong to the same polar triangle as the two silver atoms coordinated by the sulphur atom S_B of the same ligand. The two polar triangles are accordingly connected to each other by $Ag-S_B-C-S_A-Ag$ bridges. One question which arises is then why the two polar triangles are situated so closely to each other as they in fact are. This and some other problems of particular interest in connection with it will be discussed later.

Each silver atom is coordinated by three sulphur atoms, namely two atoms S_B and one atom S_A. The $Ag-S$ bond distances vary from 2.43 to 2.56 Å. It can be noticed that for each silver atom the bond distance to S_A, which has single coordination, is shorter than those to the atoms S_B, which have twofold coordination. As is seen from Table 4 the difference between the $Ag-S_A$ and $Ag-S_B$ distances is not significant in all cases. The mean distance $Ag-S_A$, 2.45 Å, is, however, appreciably shorter than the corresponding $Ag-S_B$ distance, 2.51 Å.

Three-coordinated Ag(I) has been shown to occur in some compounds related to the present one, for instance in silver(I) diethyldithiocarbamate [2] and silver(I) dipropylmonothiocarbamate.[7] In the crystal structure of bis-(thiourea)silver(I) chloride, $Ag[SC(NH_2)_2]_2Cl$, recently reported by Vizzini and Amma,[23] each of the two independent silver atoms coordinate three sulphur atoms and in addition a more distant chlorine atom ($Ag-Cl$ 2.85 and 3.04 Å). As in silver(I) dipropyldithiocarbamate there are two kinds of sulphur atoms, one coordinating two silver atoms and the other coordinating one. In the $Ag-S-Ag$ bridges the $Ag-S$ distances vary from 2.48 to 2.58 Å (average 2.54 Å), while the distances from the silver atoms to the terminal sulphur atoms are 2.43 and 2.49 Å (average 2.46 Å). As is seen these values agree well with those found in silver(I) dipropyldithiocarbamate. Similar $Ag-S$ distances have also been found in silver(I) diethyldithiocarbamate,[2] and in silver(I) dipropylmonothiocarbamate.[7] Among other compounds containing silver and sulphur the following may be mentioned (the $Ag-S$ distances are given in parentheses) AgSCN [24] (2.43 Å), $NH_4Ag(SCN)_2$[25] (2.47 Å), $[Ag_3S][NO_3]$ [26] (2.41 and 2.55 Å).

The short distances ($\sim$2.5 Å) mentioned above probably correspond to covalent $Ag-S$ bonds. Some appreciably longer $Ag-S$ bond distances have, however, been found in $AgSCN \cdot P(C_3H_7)_3$,[27] namely 2.83 and 2.88 Å. In monothiosemicarbazidesilver(I) chloride recently reported by Gaspari *et al.*[28] there are four short $Ag-S$ distances (2.48—2.51 Å) and one long (2.77 Å). Two distances of this kind are also found in silver(I) diethyldithiocarbamate [2] (2.70 and 2.99 Å) and in Ag_3AsS_3[21] (2.76 and 2.96 Å). In both of these compounds silver has threefold and fourfold coordination and the long distances occur at the fourcoordinated silver atoms.

Concerning the angles of coordination it is seen (Table 4b) that the angles S_A-Ag-S_B have considerably higher values (average 127°) than those of S_B-Ag-S_B (average 100°). The silver coordination is thus not quite regular. The coordination is further not planar. The distance from the silver atom to the plane of the three sulphur atoms is 0.22 Å (Ag_I), 0.38 Å (Ag_{II}), and 0.42 Å (Ag_{III}). In all cases the silver atoms are situated inside the plane of the three

coordinating sulphur atoms, *i.e.* on the same side of the plane as the centre of the molecule. This may be of interest when considering the short metal-metal distances.

The C—S—Ag angles vary from 95° to 115°. On closer inspection it is, however, seen that the variation in the C—S_A—Ag angles is rather small (99°, 101° and 104°). The average value of the two C—S_B—Ag angles for each ligand also has little variation. These mean values are for the three ligands I, II, III, 103°, 107°, and 105°. For each of the ligands one of the two C—S_B—Ag angles has a considerably higher value than the other. The two C—S_B—Ag angles of a ligand would have been equal if the ligand had been attached in a quite symmetrical way to the corresponding "equatorial" triangle of the central silver octahedron. The deviations that are in fact found in the angles considered are probably due to packing effects. The C—S—Ag angles actually have values that are very similar to those of the C—S—Cu angles in copper(I) diethyldithiocarbamate [3] the corresponding angles of which are 102°, 104°, and 113°. The Ag—S_B—Ag angles range from 88° to 105° (average 97°). In bis(thiourea)silver(I) chloride [23] Ag—S—Ag angles of 77° and 133° are found. The metal-sulphur-metal angles in $(C_2H_5)_2NCS_2Cu$ [3] are, however, 72°. Evidently angles of this type can have highly varying values in different structures.

The dithiocarbamate ligands. The interatomic distances and angles in the dithiocarbamate ligands are presented in Table 5; see also Fig. 1. The average values are given to the right in the table. As is seen from the standard deviations of the distances and angles the accuracy of the values is not high enough to permit any far reaching conclusions regarding the bonding conditions. Anyhow the mean values agree well with those reported by other authors as shown in Table 8. In this table the bonds between the nitrogen atom and the propyl carbons N—C_{A1} and N—C_{B1} are designated N—C. The bond between the dithiocarboxyl carbon and the nitrogen atom is denoted C=N to indicate the double bond character of the latter. As is found in several other dithiocarbamates the $S_A S_B CNC_{A1} C_{B1}$ part of each of the ligands is practically planar which is in accordance with the indicated double bond character mentioned above. The deviations of the atoms from the least squares planes for each ligand are given in Table 9. In addition to these deviations the distances of the atoms C_{A2} and C_{B2} to the corresponding planes are also listed. It is seen that in the ligands I and II these atoms are situated on opposite sides of the $S_A S_B CNC_{A1} C_{B1}$ plane and are thus in *trans* position relative to it. On the other hand C_{A2} and C_{B2} in ligand III are in *cis* position to the corresponding plane. Both of these configurations have been found in other dithiocarbamates studied at this institute. The actual orientation of the propyl chains is probably due to packing conditions.

The propyl groups IA, IB, IIB, IIIA, and IIIB (exception IIA) form with their nitrogen neighbours almost planar zig zag chains. The planes of these chains are not far from perpendicular to the corresponding $S_A S_B CNC_{A1} C_{B1}$ planes. The deviations of the atomic positions from the N—C—C—C planes are less than 0.07 Å. This is true even for the least squares positions (given in parentheses in Table 2) of the atoms C_{IIB2} and C_{IIIB2}. The positions of these atoms have been corrected by geometrical calculations in order to obtain

acceptable distances and angles in the alkyl chains. By these calculations the atoms have been placed strictly into the planes of their neighbours. The corrected positions fall well within high regions of the electron density peaks of these atoms.

In contrast to the propyl groups mentioned above the group IIA does not form a planar zig zag chain with its nitrogen neighbour. The chain $N_{II}C_{IIA1}C_{IIA2}C_{IIA3}$ is bent (see Fig. 3) and non-planar. According to the standard deviations given in Table 5 the distances and angles in the chain are, however, quite reasonable. On calculating a position of the atom C_{IIA3} corresponding to a planar zig zag chain it was found that in this calculated position the atom C_{IIA3} would come very close (shortest distance 2.98 Å) to atoms in an adjacent hexamer. Thus the actual configuration of the chain $N_{II}C_{IIA1}C_{IIA2}C_{IIA3}$ is probably due to packing conditions. In the electron density distribution there is no indication of an atom at the geometrically calculated position of this atom.

The difficulties connected with some of the atoms in the propyl chains are probably due to disorder phenomena which are also encountered in some other dithio- and monothiocarbamates studied at this institute. These disturbances are reflected in the temperature factors which have the highest values for the outermost carbon atoms. These are the ones which would be most easily affected by disorder effects. The peaks in the electron density distribution corresponding to these atoms are also less sharp than those corresponding to the inner atoms of the ligands. Even if the coordinates of some of the carbon atoms in the alkyl groups are somewhat uncertain, there is no doubt about the general shape and orientation of the propyl chains. The exact position of these atoms is, however, of little chemical interest.

GEOMETRICAL DEPENDENCES

In the following treatment some comments will be made on the angles and distances in the structure, applying a relation formulated by Hesse.[3] The rule, which can be used for the discussion of models of atomic arrangements, is written

$$F = S + D - A$$

Table 8. Comparison of bond distances in various dialkyldithiocarbamates. Mean values of the bonds in the dithiocarbamate groups.

Dithiocarbamate	S−C (Å)	C=N (Å)	N−C (Å)	Reference
Cu(I) diethyl	1.71	1.41	1.48	3
Tl(I) dipropyl	1.70	1.36	1.48	4
Cs(I) dibutyl	1.74	1.34	1.49	5
Cu(II) diethyl	1.72	1.34	1.47	29
Ni(II) diethyl	1.71	1.33	1.49	30
Zn diethyl	1.73	1.33	1.47	31
Zn dimethyl	1.72	1.35	1.47	32
Ni(II) dipropyl	1.71	1.33	1.47	33
Ag(I) dipropyl	*1.71*	*1.38*	*1.50*	—

Table 9. Deviations (in Ångström units) from least squares planes defined by the atoms S_A, S_B, C, N, C_{A1}, and C_{B1} with all weights equal.

Ligand	I	II	III
Atom			
S_A	0.06	−0.09	0.03
S_B	0.02	0.10	0.06
C	−0.10	−0.02	−0.13
N	0.00	−0.02	0.03
C_{A1}	−0.01	0.12	0.03
C_{B1}	0.03	−0.11	−0.01
C_{A2}	−1.47	−1.17	−1.32
C_{B2}	1.51	1.30	−1.46
Ag	0.00	−0.31	−0.83
(0,0,0	−0.12	−0.71	−1.15)

where F is the number of degrees of freedom of the model when its position and orientation in space are disregarded. S is a *symmetry* constant, the values of which are tabulated in the paper cited.[3] For an isolated group of atoms $S = -6$ when there is no symmetry in the arrangement and $S = -3$ when the only element of symmetry is an inversion centre, $\bar{1}$. The term D is determined by the *distribution* of the atoms on general or special positions applying the postulated symmetry. D is equal to the number of the position coordinates which are variable when only the symmetry and point distribution are taken into consideration. A is a reduction in the degrees of freedom due to *additional* postulated properties of the model. In most cases of interest A is equal to the number of independent geometrical elements (distances and angles) which are postulated to be fixed in the model.

The degrees of freedom of a model are of particular interest when discussing *geometrical dependences* in a structure. In a given model with F degrees of freedom consider a set of geometrical elements (distances and angles) the values of which have not been postulated. Let C be the number of these unpostulated elements under consideration. Then if $C > F$, there are geometrical dependences among the considered elements, *i.e.* the values of some or all of the distances and angles under consideration are interdependent and/or dependent on the postulated properties of the model.

Now let us study a *model* of the central part of the silver(I) dipropyldithiocarbamate hexamer comprising the silver atoms and the dithiocarboxyl groups. Postulating a centre of symmetry for the model, the symmetry constant S will be equal to -3. The atoms are distributed on general positions and the asymmetric unit consists of twelve atoms (three silver, six sulphur, and three carbon atoms) each with three variable coordinates. Accordingly $D = 12 \times 3 = 36$. If no further assumptions are made $A = 0$ and thus $F = -3 + 36 + 0 = 33$.

In the following discussion 42 geometrical elements in the asymmetric unit of the model will be taken into consideration. All of them will be considered either as postulated or as unpostulated properties. Three of them correspond to the short Ag—Ag distances in the crystal structure and the

others to bond distances and angles in Tables 4 and 5. All of them are of particular interest for the discussion of the structure. The postulated values can, but need not necessarily, be those given in the tables. The elements thus considered in the asymmetric unit of the model are, three Ag—Ag, nine Ag—S, and six C—S distances, and nine S—Ag—S, three Ag—S—Ag, nine C—S—Ag, and three S—C—S angles. If none of the values of these 42 geometrical elements is postulated, $C=42$ and $F=33$. Thus C exceeds F by nine units and there are evidently geometrical dependences among the considered elements in the model.

The geometrical dependences among the 42 angles and distances which here are taken into consideration are more easily seen if the degrees of freedom are successively reduced by introducing a number of postulates. The demonstration of the dependences can for instance be done in the following way:

1. Let us postulate the dithiocarboxyl groups to be rigid, *i.e.* the six C—S distances and the three S—C—S angles are fixed. Let further the nine Ag—S coordination distances be fixed. The number of postulated geometrical elements is then: $A=6+3+9=18$. Accordingly $F=-3+36-18=15$. The number of unpostulated geometrical elements under consideration, C, is now 24 and thus still exceeds the number of degrees of freedom by nine units.

2. Let us further postulate the nine C—S—Ag angles to be fixed. Then $A=27$ and $F=6$. The group of considered geometrical elements which are still unpostulated now comprises nine S—Ag—S angles, three Ag—S—Ag angles, and three Ag—Ag distances, *i.e.* $C=15$. Since $F=6$ not more than six of these fifteen elements can have independent values.

The remaining six degrees of freedom can for instance be used up in the following way:

3. The values of six of the S—Ag—S coordination angles are postulated. The model is now rigid, since the number of degrees of freedom, F, is zero. This rigid model can be built in a very limited number of alternative ways but for each of these alternatives the remaining geometrical elements under consideration (three S—Ag—S and three Ag—S—Ag angles and three Ag—Ag distances) are fixed. The three unpostulated S—Ag—S angles which in this way are geometrically determined by the prescribed properties of the model can have values which considerably differ from the postulated ones. The postulations made in this manner may thus result in marked irregularities in the silver coordination. The possible values of the Ag—Ag distances and the Ag—S—Ag angles also follow from the prescriptions. In this particular model the metal-metal distances are accordingly determined by the values which are given to other geometrical elements in the arrangement.

In the same way the short Ag—Ag distances in the *crystal structure* can be the result of requirements from other geometrical elements to obtain favourable values. If so, or if the contrary cannot be proved, one is not permitted to draw any conclusions about the bond conditions from the occurrence of these short metal-metal distances. The fact that the silver atoms are situated inside the corresponding planes of the coordinating sulphur atoms, which might have been ascribed to metal-metal bond interactions, can as well be the geometrical result of other features in the structure. In this connections it also deserves mentioning that in the alkali halides KF, KCl, RbCl, and RbBr the

metal-metal distances are shorter than those in the corresponding metals. The short metal-metal distances in these compounds can be ascribed to the metal-ligand linkage.

The angles and distances postulated in the discussion of the model have reasonable values in the crystal structure. It is then quite possible that they determine the shape of the central part of the molecule and thus also the metal-metal distances. Still, the values of these angles and distances are certainly not independent of other features in the general arrangement. The model studied above only corresponds to the central part of a hexamer. This part is, however, not isolated in the crystal structure and the angles and distances in it are probably influenced by steric restrictions connected with the packing of the large ligands in the periodic arrangement. In fact, the structure as a whole has to be regarded as a compromise where contradicting tendencies have to be balanced against each other in order to make the arrangement geometrically possible.

As is seen one cannot draw definitive conclusions from isolated distances and angles in a crystal structure without making sure that the values of the distances and angles under consideration are not geometrically influenced or determined by the values of other geometrical elements which may be of equal or greater importance.
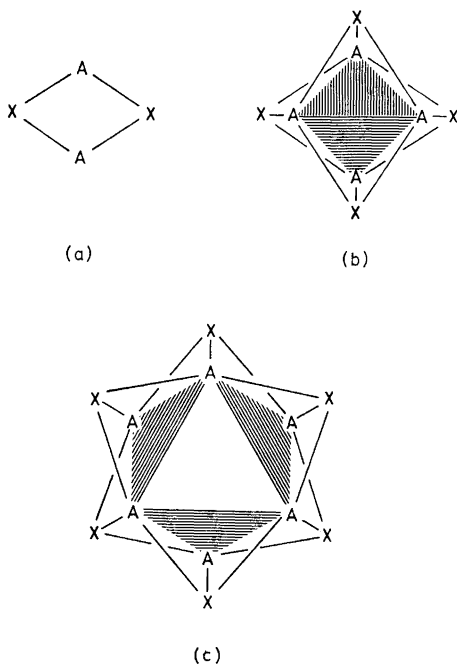

(a)   (b)

(c)

Fig. 6. The linkage in some AX-polymers:
a) dimer, b) tetramer, c) hexamer.

THE LINKAGE IN SOME AX-POLYMERS

Compounds of the composition AX, where A is a metal atom and X is a bulky ligand, generally appear as polymers in the solid state. Some of them are high polymers as caesium(I) dibutyldithiocarbamate,[5] which has a layer structure and thallium(I) dipropyldithiocarbamate,[4] where the structural units are arranged in chains. The majority of the compounds studied by the present research group, however, occur as discrete low polymers, $(AX)_n$. The degree of polymerity, n, hitherto found for the compounds in question, has been 2, 4, and 6. The linkage between the metal atoms, A, and the ligands, X, in the simplest of these low polymers is illustrated in Fig. 6 a—c.

In the dimer there is a central metal pair. Each metal atom, A, is linked by two X and each X by two A. This principle is represented in the structure of gold(I) dipropyldithiocarbamate [2] and probably also in some other gold(I) dialkyldithiocarbamates under investigation. It is also found in diazoamino-benzene copper(I) [34] and in silver(I) perfluorobutyrate,[35] C_3F_7COOAg.

The metal atoms in the tetramer (Fig. 6 b) form a central tetrahedron and the four ligands are situated outside the faces of this. In this case each A is linked by *three* X and each X by *three* A. This is the simplest type of tetramer $(AX)_4$ in which the metal atoms are linked by more than two ligands. This type of linkage appears in copper(I) diethyldithiocarbamate [3] and also in some other compounds, for instance $TlOCH_3$ [36] and $LiCH_3$.[37] It should be mentioned that the same type of $A-X$-linkage is also found in some $(AXR_n)_4$ compounds, for instance $(C_2H_5)_3AsCuI$ [38] (A=Cu, X=I), and $(CH_3)_3PtCl$ [39] (A=Pt, X=Cl), in which metal tetrahedra also occur. In these tetramers there are, however, additional ligands, (R), situated outside the metal tetrahedron. The molecular structure of $(CH_3)_3PtCl$ could also be regarded as an anti-type to that of copper(I) diethyldithiocarbamate. Thus there is a tetrahedron of chlorine atoms with $Pt(CH_3)_3$ groups situated outside its faces.

In the hexamer, seen in Fig. 6 c, the six metal atoms, A, form an octahedron. The six ligands, X, are situated outside six of the eight faces of this octahedron. As in the tetramer each A is linked by *three* X and each X by *three* A. This arrangement represents the simplest and most regular hexamer, in which the metal atoms are linked by more than two ligands. This type of linkage is represented by silver(I) dipropyldithiocarbamate, described in this paper, and by silver(I) dipropylmonothiocarbamate,[7] and copper(I) dipropylmono-thiocarbamate.[8]

Other types of AX-hexamers are, however, also known. In the rhombo-hedral phase of silver(I) fulminate,[20] for instance, the metal atoms and ligands form a twelve membered ring by the repetition of the sequence $-Ag-C-Ag-C-$. The oxygen atoms do not take part in the linkage within the rings but these are apparently connected to each other by $Ag-O$ interactions. The crystal structure of silver(I) diethyldithiocarbamate [2] can be regarded as a borderline case between a chain structure and an arrangement with discrete hexameric molecules. There is considerable interaction between the hexamers, which are arranged in strings in the structure. The metal atoms in the hexamers form doubly bent chains. Each silver atom has threefold coordination as in silver(I) dipropyldithiocarbamate but the ligands are linked by

varying numbers (2, 3, or 4) of metal atoms. The irregularities in the linkage are probably due to the interaction between the hexamers. This interaction is reflected by the fact that the compound is only sparingly soluble in organic solvents. On the contrary silver(I) dipropyldithiocarbamate which forms regular hexamers is readily soluble in several similar solvents.

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