

The Crystal and Molecular Structure of the Silver(I) Dipropylmonothiocarbamate Hexamer

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The crystal structure of silver(I) dipropylmonothiocarbamate, $(C_3H_7)_2NCOSAg$, has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/a$. Unit cell parameters are $a = 13.313 \text{ \AA}$, $b = 19.904 \text{ \AA}$, $c = 11.901 \text{ \AA}$, $\beta = 93.28^\circ$. The structure consists of isolated $[(C_3H_7)_2NCOSAg]_6$ hexamers. There are two hexameric molecules in the unit cell. The silver atoms form an almost regular central octahedron in the molecule. The metal-metal distances are somewhat larger than those of the metallic phase of silver. Outside six of the faces of the octahedron a monothiocarbamate ligand is situated, linked to the silver octahedron by metal-sulphur and metal-oxygen bonds. Each oxygen atom is linked to one silver atom and each sulphur atom to two silver atoms. The silver atoms have threefold, non-planar coordination. The metal atoms are situated inside the plane of the coordinated atoms.

The structure of the title compound is compared to those of related compounds with particular reference to the geometry of the linkage and to the factors governing the metal-metal distances and the metal coordination. The degree of polymerization and the packing of the molecules are also discussed.

The determination of the crystal structure of silver(I) dipropylmonothiocarbamate forms part of a series of crystal studies on $(AX)_n$ compounds carried out by this research group. A represents an alkali metal, a univalent coinage metal or a univalent thallium atom; X is a dialkyldithiocarbamate, a dialkylmonothiocarbamate or a thiolate group; and n is the degree of polymerization. The compounds of this type are either high polymers with layer-¹ or chain-type² structures or low polymers. There are also marginal cases.³ In crystal structures consisting of isolated low polymeric units, cases of n equal to 2, 4, and 6 have been encountered. The hexamers studied so far are copper(I) dipropylmonothiocarbamate,⁴ silver(I) dipropyldithiocarbamate,⁵ and silver(I) dipropylmonothiocarbamate (this paper). Comparisons of these three compounds will be made in the following discussion along with a presentation of the structure of silver(I) dipropylmonothiocarbamate. The shorthand notations $CuDnPMTC$, $AgDnPDTC$, and $AgDnPMTC$ will be used. Reference will also be made to the tetrameric copper(I) diethyldithiocarbamate, $CuDEDTC$.⁶

EXPERIMENTAL

Crystals of silver(I) dipropylmonothiocarbamate, $[(C_3H_7)_2NCOSAg]_n$, were supplied by Åkerström, who had prepared them according to his method.⁷ The crystals were obtained from ligroin and benzene as light yellow rods with the rod axis parallel to the [001] direction. Their density was measured by flotation using an aqueous solution of K_2HgI_4 . The unit cell parameters were determined from a Guinier-Hägg powder photograph taken, using $CrK\alpha_1$ radiation and elementary silicon as a calibrant ($a = 5.4305 \text{ \AA}$). Unit cell and symmetry data are given in Table 1.

Table 1. Unit cell and symmetry.

Formula unit: $(C_3H_7)_2NCOSAg$
 Crystal system: monoclinic.
 Unit cell parameters: $a = 13.313 \text{ \AA} \pm 0.005$,
 $b = 19.904 \text{ \AA} \pm 0.008$,
 $c = 11.901 \text{ \AA} \pm 0.005$,
 $\beta = 93.28^\circ \pm 0.03$.
 Volume of unit cell: 3148 \AA^3 .
 Density (measured): 1.697 g cm^{-3} .
 Number of formula units per unit cell: 12.
 Density (calculated): 1.676 g cm^{-3} .
 Diffraction symmetry: $2/m$.
 Systematic absences: $h0l$ for $h = 2n + 1$,
 $0k0$ for $k = 2n + 1$.
 Space group: $P2_1/a$.
 Coordinates of equivalent positions:

x, y, z	$\bar{x}, \bar{y}, \bar{z}$
$\frac{1}{2} + x, \frac{1}{2} - y, z$	$\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$

The X-ray reflexions were recorded on equi-inclination Weissenberg photographs, using $CuK\alpha$ radiation. 1091 independent reflexions in the layers $0 \leq l \leq 9$ were recorded, using [001] as the rotation axis. The crystals were found to decompose in the X-ray beam, so each crystal could be used for the recording of one layer only. Details of the crystals are given in Table 2. The relative intensities of the reflexions were estimated

Table 2. Crystals.

Crystal	Dimensions (mm) ^a	Layer recorded	Number of reflexions
1	$0.085 \times 0.048 \times 0.040$	$hk0$	91
2	$0.084 \times 0.060 \times 0.044$	$hk1$	176
3	$0.090 \times 0.048 \times 0.044$	$hk2$	173
4	$0.120 \times 0.042 \times 0.036$	$hk3$	192
5	$0.090 \times 0.044 \times 0.038$	$hk4$	129
6	$0.069 \times 0.039 \times 0.032$	$hk5$	74
7	$0.083 \times 0.035 \times 0.032$	$hk6$	92
8	$0.072 \times 0.045 \times 0.037$	$hk7$	38
9	$0.104 \times 0.040 \times 0.030$	$hk8$	56
10	$0.168 \times 0.060 \times 0.044$	$hk9$	70
11	$0.032 \times 0.032 \times 0.026$	$h1l$	18
12	$0.048 \times 0.048 \times 0.039$	$h2l$	27

^a The extension in the direction of the rotation axis is given first.

visually, using calibrated intensity scales. The multiple film technique was employed, using six films. Corrections were made for Lorentz and polarization effects but not for absorption and extinction.

Interlayer scale factors were determined from data obtained by recording the two layers $h1l$ and $h2l$. One crystal was used for each layer, being rotated about the axis [010]. Details of these crystals are also given in Table 2. The calculations of the interlayer scale factors were based on the measurement of 45 reflexions. Only small changes in these values were noticed when the individual scale factors were included in the final refinement.

DETERMINATION OF THE ATOMIC POSITIONS

Approximate positions of the silver atoms were determined from the three-dimensional Patterson function. The positions of the sulphur, oxygen, nitrogen and carbon atoms were determined by successive three-dimensional difference syntheses. The coordinates of the silver, sulphur, and oxygen atoms were repeatedly adjusted by three-dimensional Fourier syntheses using the backshift technique. No attempt was made to locate the hydrogen atoms. The coordinates and isotropic temperature factors of all but the hydrogen atoms were refined by the method of least squares using a full matrix programme. The ten scale factors were also included in the refinement. In the expression minimized, $\sum \omega (|F_o| - |F_c|)^2$, the weights ω were calculated according to the equation suggested by Cruickshank *et al.*⁹ $\omega = 1/(a + |F_o| + c|F_c|^2 + d|F_c|^3)$. The constants used in the final cycles were $a = 5.0$, $c = 0.0015$, $d = 0.00005$. Atomic scattering factors for the elements were obtained from Hanson *et al.*¹⁰ The real part of the dispersion correction for silver was introduced into the calculations.¹¹ The least squares calculations were continued until the shifts on the parameters were less than one tenth of the estimated standard deviations. At this stage the discrepancy index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.108. The atomic coordinates and isotropic temperature factors from the last cycle of the refinement are given in Table 3. When anisotropic temperature factors were introduced into the refinement, the index R decreased to 0.098. The shifts on the atomic coordinates were negligible, however.

For the nine carbon atoms marked by asterisks in Table 3, the positions obtained from the least squares refinement result in interatomic distances and angles which were considered to deviate too much from their expected values. The least squares parameters for these atoms are therefore presented within parentheses in this table. The corresponding positions, given without parentheses, were determined from geometrical calculations in combination with considerations of the electron density distribution. The accuracy of the positions of these atoms is thus not high, although the bonding distances and angles are reasonable. Furthermore, no atoms are closer to one another than the van der Waals distances, unless connected by covalent bonds. The R -value corresponding to the adjusted positions is 0.118. The low accuracy of the positions of certain of the atoms could be due to disorder phenomena but is probably also caused by errors in the intensity data. Particularly, no corrections have been made for absorption and extinction. It has not been the aim of this investigation, however, to obtain detailed information on the bonding conditions within the ligands. No doubt remains as to the general shape and orientation of the ligands. Accordingly, the accuracy obtained is regarded as satisfactory for the present purpose.

Table 3. Atomic parameters and standard deviations. The parameters of all atoms, except 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. The least squares parameters of these atoms are given in parentheses. The coordinates of the atoms with the notation I, II, and III can be obtained from those given in the table by reversing the signs of the coordinates.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	$B \text{ \AA}^2$	$\sigma(B) \text{ \AA}^2$
Metal atoms								
Ag _I	0.1523	0.0003	-0.0101	0.0002	-0.0576	0.0003	5.85	0.12
Ag _{II}	0.0506	0.0003	0.0696	0.0002	0.1329	0.0003	5.60	0.12
Ag _{III}	-0.0321	0.0003	0.0777	0.0002	-0.1318	0.0003	6.10	0.13
Monothiocarbamate ligand I								
S _I	0.0361	0.0010	-0.1597	0.0007	-0.0216	0.0012	6.0	0.3
O _I	0.211	0.003	-0.118	0.002	-0.096	0.003	7.8	0.8
C _I *	0.159		-0.167		-0.071			
	(0.148)	0.005	-0.172	0.003	-0.076	0.005	9.4	1.6)
N _I	0.199	0.003	-0.227	0.002	-0.085	0.004	7.3	1.0
C _{IA1}	0.297	0.004	-0.238	0.003	-0.117	0.005	8.3	1.4
C _{IA2}	0.281	0.005	-0.251	0.003	-0.248	0.007	12.0	2.0
C _{IA3}	0.389	0.007	-0.259	0.005	-0.301	0.008	15.9	2.8
C _{IB1}	0.150	0.004	-0.293	0.002	-0.045	0.005	7.3	1.3
C _{IB2}	0.181		-0.302		0.079			
	(0.163)	0.007	-0.344	0.005	0.097	0.008	14.1	2.8)
C _{IB3}	0.151		-0.374		0.113			
	(0.189)	0.010	-0.297	0.007	0.099	0.012	20.6	4.7)
Monothiocarbamate ligand II								
S _{II}	-0.1152	0.0010	-0.0501	0.0006	0.2358	0.0011	5.8	0.3
O _{II}	-0.019	0.003	0.056	0.002	0.311	0.003	7.6	0.9
C _{II} *	-0.091		0.015		0.335			
	(-0.104)	0.006	0.028	0.003	0.389	0.006	9.8	1.9)
N _{II}	-0.158	0.008	0.012	0.005	0.429	0.009	19.4	3.3
C _{IIA1}	-0.105		0.067		0.493			
	(-0.095)	0.004	0.078	0.003	0.504	0.004	7.1	1.2)
C _{IIA2}	-0.155	0.006	0.138	0.004	0.462	0.007	13.6	2.3
C _{IIA3}	-0.121	0.006	0.187	0.004	0.554	0.008	13.5	2.4
C _{IIB1}	-0.261	0.005	-0.015	0.003	0.442	0.005	8.4	1.4
C _{IIB2} *	-0.255		-0.079		0.513			
	(-0.199)	0.007	-0.061	0.004	0.511	0.007	14.7	2.6)
C _{IIB3}	-0.360		-0.110		0.514			
	(-0.327)	0.005	-0.107	0.004	0.521	0.006	12.2	2.1)
Monothiocarbamate ligand III								
S _{III}	-0.2292	0.0010	-0.0382	0.0006	-0.1196	0.0011	5.8	0.3
O _{III}	-0.189	0.003	0.071	0.002	-0.235	0.003	7.8	0.9
C _{III}	-0.255	0.004	0.040	0.002	-0.197	0.004	6.4	1.2
N _{III}	-0.346	0.004	0.049	0.002	-0.223	0.004	9.1	1.3
C _{IIIA1} *	-0.375		0.107		-0.304			
	(-0.378)	0.007	0.112	0.005	-0.311	0.009	17.2	3.1)
C _{IIIA2} *	-0.390		0.167		-0.225			
	(-0.389)	0.006	0.168	0.004	-0.193	0.007	13.2	2.3)
C _{IIIA3}	-0.410	0.010	0.223	0.007	-0.311	0.013	24.7	4.9
C _{IIIB1}	-0.442	0.005	0.020	0.003	-0.166	0.005	9.1	1.6
C _{IIIB2}	-0.496	0.006	-0.030	0.004	-0.230	0.007	13.4	2.3
C _{IIIB3}	-0.582	0.011	-0.057	0.006	-0.174	0.011	21.8	4.1

COMPUTATION

All the calculations have been carried out on a CD 3600 computer at Uppsala Data Central. The following programmes were used (all the programmes are written in Fortran IV).

Programmes	Authors
Least squares refinement of unit cell dimensions	J. Tegenfeldt, Uppsala, Sweden
Lorentz-polarization corrections, Fourier summations, structure factor calculations	A. Zalkin, Berkeley, U.S.A., modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden
Least squares refinement of positional parameters and temperature factors	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A., modified by C.-I. Brändén, R. Liminga and J.-O. Lundgren, Uppsala, Sweden
Interatomic distances and angles	A. Zalkin, Berkeley, U.S.A
Perspective illustrations	C. K. Johnson, Oak Ridge, U.S.A.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Notation. The silver atoms and monothiocarbamate ligand atoms in the chosen asymmetric unit, for which the coordinates are given in Table 3, are denoted by I, II, and III, respectively. The carbon atoms in the propyl chains are given additional notation according to Fig. 1. The propyl chains A and B

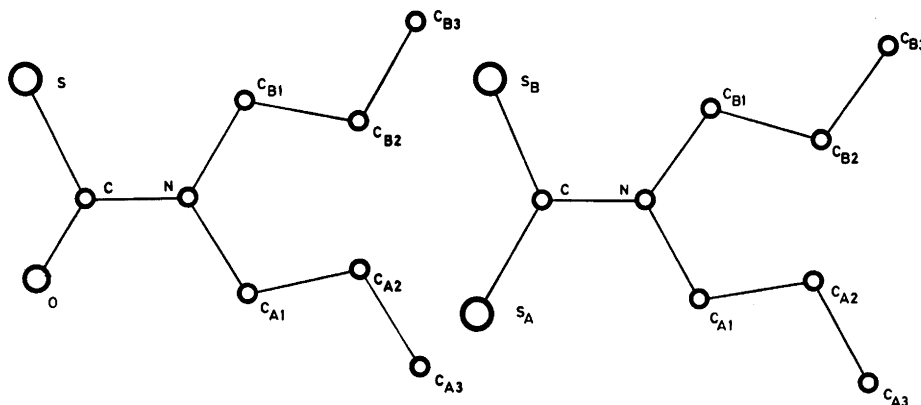


Fig. 1. The monothiocarbamate (left) and dithiocarbamate (right) ligands showing notation of atoms.

correspond to the oxygen and sulphur atoms as is shown in this figure. The atoms related to the atoms in the asymmetric unit by a centre of symmetry at the origin are denoted by a bar above the notation, e.g. $\overline{C_{III B2}}$

General features. The structure is made up of discrete, centrosymmetric, hexameric molecules, $[(C_3H_7)_2NCOSAg]_6$. There are two such molecules in the unit cell with their centres at $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$. The molecules in the structure are related to one another by screw axes and glide planes. The molecular arrangement is shown in Fig. 2. Each molecule consists of a central, almost

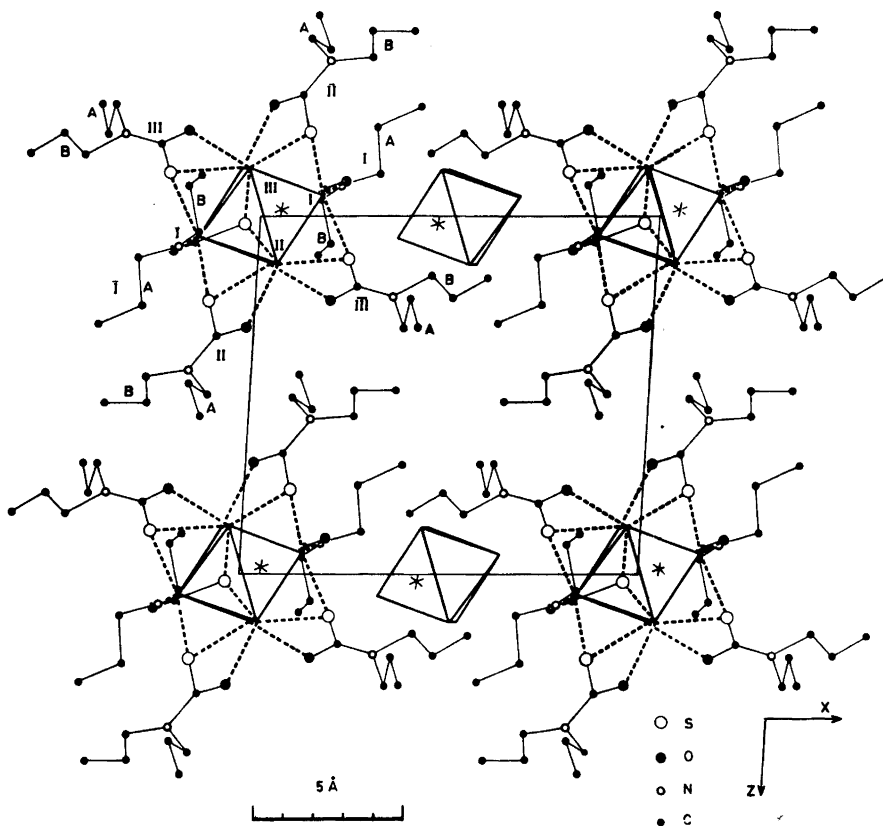


Fig. 2. Projection on the xz -plane showing the arrangement of the molecules in the crystal structure. For the sake of clarity, only the metal octahedra are drawn for the molecules with their centres at $(\frac{1}{2}, \frac{1}{2}, 0)$. The visible polar faces of the octahedra are marked by stars (*cf.* Fig. 3). The two molecules in the unit cell can be related by a screw axis perpendicular to the plane of projection and intersecting it at $(1/4, 0, 0)$.

regular octahedron of silver atoms and an outer region of monothiocarbamate ligands. The bulky organic ligands effectively shield the metal group in the hexameric unit from interaction with neighbouring molecules in the crystal. The forces acting between different molecules are thus of van der Waals type. Intermolecular distances shorter than 4 Å are given in Table 4.

The arrangement of the molecules in AgDnPMTc is analogous to that found in the crystal structure of CuDnPMTc.⁴ The two structures belong to

Table 4. Intermolecular distances shorter than 4 Å. Only the geometrical positions are used for the atoms, which have been geometrically corrected (*cf.* Table 3). The relationship of the coordinates for the atoms in the second column to those given in Table 3 (coord. x, y, z) is expressed by one of the following symbols, corresponding to a symmetry operation:

$s_0: x, y, z$ $s_1: -x, -y, -z$ (centre of symmetry)

$s_2: \frac{1}{2} + x, \frac{1}{2} - y, z$ (glide plane) $s_3: \frac{1}{2} - x, \frac{1}{2} + y, -z$ (screw axis).

The additional symbols $\pm a$, $\pm b$, $\pm c$ indicate a translation of one identity period in the positive (negative) direction of the a , b , c axis, respectively.

Atoms			Dist. (Å)	Atoms			Dist. (Å)
S _I	O _{III}	s_1	3.98	O _{III}	C _{IIA₂}	$s_0 - c$	3.90
S _I	C _{IIA₁}	$s_2 - a - b$	3.90	O _{III}	C _{IIA₂}	$s_0 - c$	3.56
S _{II}	O _I	s_1	3.92	N _{II}	C _{IIA₁}	$s_1 + c$	3.90
S _{II}	C _{IB₂}	$s_2 - a - b$	3.68	C _{II}	C _{IIA₁}	$s_1 + c$	3.62
S _{III}	C _{IB₁}	$s_2 - a - b$	3.85	C _{IA₂}	C _{IIA₁}	s_1	3.72
S _{III}	C _{IB₂}	$s_2 - a - b$	3.71	C _{IA₂}	C _{IIIA₂}	$s_3 - a - b$	3.88
O _I	O _{II}	s_1	3.73	C _{IB₂}	C _{IIIB₁}	$s_3 - a - b$	3.58
O _I	C _{II}	s_1	3.79	C _{IB₂}	C _{IIIB₂}	$s_3 - a - b$	3.85
O _I	C _{III}	s_1	3.82	C _{IB₂}	Ag _I	$s_3 - b$	3.85
O _I	C _{IIIB₂}	$s_0 + a$	3.20	C _{IIA₁}	C _{IIA₁}	$s_1 + c$	3.87
O _{II}	O _{III}	s_1	3.90	C _{IIA₂}	C _{IIIA₂}	$s_2 + c$	3.64
O _{II}	C _I	s_1	3.99	C _{IIIB₁}	C _{IIIB₂}	$s_1 - a$	3.98
O _{II}	C _{IIA₁}	$s_1 + c$	3.71	C _{IIIB₂}	C _{IIIB₂}	$s_0 + c$	3.96
O _{III}	C _{IIA₁}	$s_0 - c$	3.49	C _{IIIB₂}	Ag _I	$s_0 - a$	3.99

the same space group and the two molecules in the unit cells are related to each other in the same way in both compounds. However, the hexameric molecules of AgDnPDTC⁵ are arranged completely differently, having triclinic symmetry and only one molecule in the unit cell. As discussed in a later section, the molecules of the two compounds AgDnPMTC and CuDnPMTC have a very similar shape, whereas the molecules of AgDnPDTC are somewhat different. The difference in packing is probably brought about by this difference in molecular shape.

The hexamer. A diagram of the centrosymmetric hexameric molecule is shown in Fig. 3. The silver atoms form a central octahedron, and the six dipropylmonothiocarbamate ligands are situated outside six of the eight faces of this octahedron. These six faces will be referred to as the "equatorial faces". The two faces not attached in this way to a ligand will be referred to as the "polar faces". In the later discussion, the edges of the polar faces will be called the "polar edges", and the remaining six edges the "equatorial edges". The projection plane of Fig. 3 is parallel to the polar faces. The orthonormalized coordinates (XYZ), given in Table 5, complement the figure for the description of the structure. The YZ -plane is parallel to the polar faces and passes through the centre of the molecule. The X -coordinate gives the deviation of the atoms from this plane. The striking regularity of the hexameric molecule is immediately seen from Fig. 3 and Table 5. The silver, sulphur, and oxygen atoms are all situated close to the six X -levels: ± 1.2 Å (Ag), ± 2.2 Å (S), ± 0.1 Å (O). It can be seen that the central part of the arrangement exhibits a close ap-

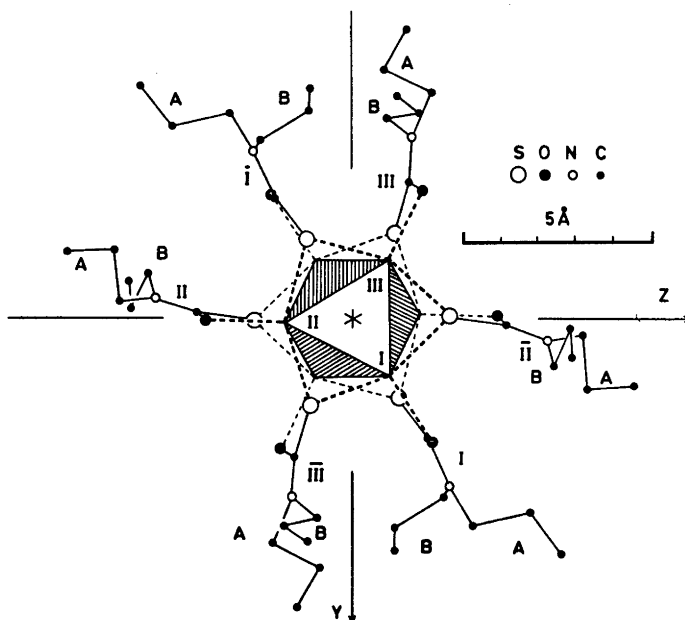


Fig. 3. Projection of the hexameric molecule on a plane parallel to the polar faces. Coordinates from Table 5. The *Y*- and *Z*-axes are parallel to, and the *X*-axis perpendicular to the plane of projection. The silver atoms are situated at the apices of the octahedron. The point where the *X*-axis intersects the visible polar face is marked by a star. Three polar and six equatorial edges are shown. The ligands I, II, and III, which are pointing upwards, are related to the ligands I, II, and III, which are pointing downwards, by a centre of symmetry in the origin.

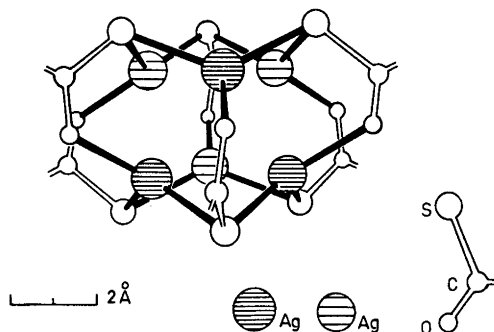


Fig. 4. Perspective illustration of the linkage in the central part of the hexameric molecule. Bonds from silver atoms to coordinating sulphur and oxygen atoms are illustrated with black lines. The silver atoms in the foreground are lined with a denser pattern than the silver atoms in the background. The directions of the ligands are indicated by short segments of the carbon-nitrogen bonds. One carbon atom is hidden behind the upper central silver atom.

Table 5. Atomic coordinates in Ångström units in the orthonormalized coordinate system, XYZ (cf. Fig. 2). The coordinates of atoms with the notation I, II, III can be obtained from those in the table by reversing the signs of the coordinates.

	X	Y	Z
Metal atoms			
Ag _I	1.21	1.52	1.00
Ag _{II}	1.21	0.12	-1.81
Ag _{III}	1.21	-1.58	1.00
Monothiocarbamate ligand I			
S _I	-2.13	2.10	1.22
O _I	0.11	3.23	2.15
C _I	-1.13	3.13	2.06
N _I	-1.71	4.36	2.62
C _{IA₁}	-1.00	5.40	3.23
C _{IA₂}	-1.06	5.01	4.77
C _{IA₃}	-0.18	6.06	5.61
C _{IB₁}	-3.20	4.71	2.45
C _{IB₂}	-3.35	5.48	1.15
C _{IB₃}	-4.77	6.08	1.11
Monothiocarbamate ligand II			
S _{II}	-2.21	0.05	-2.61
O _{II}	0.07	0.07	-3.89
C _{II}	-1.22	-0.16	-4.07
N _{II}	-2.00	-0.54	-5.24
C _{IIA₁}	-0.85	-0.43	-6.18
C _{IIA₂}	-0.10	-1.83	-6.32
C _{IIA₃}	0.74	-1.77	-7.58
C _{IIB₁}	-3.29	-1.27	-5.43
C _{IIB₂}	-4.38	-0.29	-5.87
C _{IIB₃}	-5.72	-1.02	-5.90
Monothiocarbamate ligand III			
S _{III}	-2.22	-2.28	1.14
O _{III}	0.04	-3.42	1.91
C _{III}	-1.07	-3.64	1.53
N _{III}	-1.61	-4.76	1.61
C _{IIIA₁}	-0.79	-5.94	2.14
C _{IIIA₂}	-0.15	-6.54	0.88
C _{IIIA₃}	0.74	-7.62	1.50
C _{IIIB₁}	-2.96	-5.27	0.94
C _{IIIB₂}	-4.06	-5.44	1.85
C _{IIIB₃}	-5.29	-5.86	1.21

proximation to $\bar{3}$ symmetry. It can then be expected that isolated molecules in solution have this symmetry. The deviations from $\bar{3}$ symmetry in the crystal are probably the result of packing effects.

The linkage of the ligands to the metal atoms can be seen in Fig. 3, and is more clearly illustrated in Fig. 4. The sulphur atom of the monothiocarbamate ligand is coordinated to two silver atoms and the oxygen atom to one silver atom.

In this way each ligand is attached to one equatorial face of the octahedron. It can also be seen that each silver atom coordinates three atoms, two sulphur and one oxygen. Since these atoms belong to three different ligands, there are accordingly no chelate rings in the molecule. It is shown in the figures that each silver atom is connected to two silver atoms in the same polar face by Ag-S-Ag bridges, and to two silver atoms in the other polar face by Ag-S-C-O-Ag bridges. The short bridges, involving one atom from the ligand, are thus associated with the polar edges, whereas the long bridges, involving three atoms from the ligand, are associated with the equatorial edges.

The metal-ligand linkage in AgDnPMTC is also found in CuDnPMTC and AgDnPDTC. In the latter compound, the oxygen atom is replaced by a sulphur atom (Fig. 1). This sulphur atom, referred to as S_A , is thus coordinated to only one metal atom, and the other sulphur atom, S_B , to two metal atoms.

The metal-ligand linkage in the tetrameric molecules of $[(C_2H_5)_2NCS_2Cu]_4$, CuDEDTC,⁶ is of course different from that found in the hexameric AgDnPMTC, but both the coordination around the metal atoms and the attachment of the ligands to the metal atoms are very similar. In this compound, the metal atoms form a central tetrahedron with the ligands situated outside the four faces of this tetrahedron. The ligands are attached to the triangular faces by two bonds from one sulphur atom and one bond from another sulphur atom. The common features of this tetrameric and the three hexameric molecules, CuDnPMTC, AgDnPMTC and AgDnPDTC, raise the question of which factors govern the degree of polymerization in this group of compounds. Some aspects on this question will be discussed in a later section.

A metal-ligand arrangement with certain features in common with both the copper and silver monothiocarbamates and the dithiocarbamates has been reported¹² in the very interesting structure of the anion $[(CN)_2CCS_2]_6Cu_8^{4-}$. In this complex the ligands, which closely resemble the thiocarbamates, are also attached to the faces of a central metal polyhedron, which, in this case, is a cube. Each sulphur atom of the ligand is coordinated to two copper atoms, and the ligand is accordingly linked to four metal atoms. As in the dithio- and monothiocarbamates mentioned above, the metal coordination is threefold.

Octahedral metal arrangements have been found in some other compounds, for instance in some transition metal halides, containing the structural units A_6X_{12} and A_6X_8 .¹³ These are cluster compounds with short metal-metal distances. In the A_6X_{12} group, the ligands X bridge the edges of the central A_6 -octahedron. The linkage is thus quite different from that in the hexameric silver and copper compounds, discussed in the present paper. The linkage in the A_6X_8 group does, however, have certain features in common with the dithiocarbamates and monothiocarbamates discussed here. The group can be derived from the A_6X_8 arrangement in these compounds by also attaching X ligands to the polar faces. The arrangement is naturally more complicated in the dithiocarbamate and monothiocarbamate compounds, since two atoms from each ligand are involved in the linkage.

The central octahedron. Because of the centrosymmetric nature of the arrangement there are six independent silver-silver distances in the central metal octahedron. These are given in Table 6. The average silver-silver

Table 6. Distances in Ångström units between metal atoms in the central octahedron.

Atoms	Dist.	σ	Atoms	Dist.	σ
Ag _I - Ag _{II}	3.138	0.005	Ag _I - Ag _{II}	3.037	0.005
Ag _I - Ag _{III}	3.100	0.005	Ag _I - Ag _{III}	3.141	0.005
Ag _{II} - Ag _{III}	3.281	0.005	Ag _{II} - Ag _{III}	2.943	0.005

distance is 3.11 Å, which is little different from the interatomic distance in metallic silver, 2.89 Å.¹⁴ Short silver-silver distances of comparable length to those found in AgDnPMTC have also been reported in some other compounds, as is shown in Table 7.

Table 7. A comparison of short Ag-Ag distances (Å) in some Ag(I) complexes.

AgCNO (rhomb.) ¹⁵	2.83
AgCNO (orthor.) ¹⁵	2.93
Ag ₃ AsS ₃ ¹⁶	2.95 - 3.09
AgI, C ₅ H ₁₁ N ¹⁷	2.99, 3.02, 3.09
[(C ₃ H ₇) ₂ NCS ₂ Ag] ₆ ⁵	3.02 (average value)
Ag ₂ TeO ₃ (OH) ₄ ²⁰	3.03
C ₆ H ₅ CCAgP(CH ₃) ₃ ¹⁸	3.033
[(C ₃ H ₇) ₂ NCOSAg] ₆	3.04, 3.17 (average values)
(C ₄ H ₉) ₄ NAg ₃ I ₄ ¹⁹	3.06, 3.13
Ag[SC(NH ₂) ₃] ₂ Cl ²⁰	3.132
(AgPO ₃) _x ²¹	3.15

The difference between the largest and the smallest silver-silver distance in AgDnPMTC is 0.34 Å, *i.e.* about 11 % of the average value. Since the bridging between the metal atoms is different along the polar and the equatorial edges, there is little reason to expect these edges to be equal in length. The average length of the polar and equatorial are, however, found to be 3.17 and 3.04 Å, respectively. The difference is therefore small, and is partly offset by variations within the sets. These variations are probably the result of packing effects. It can, for example, be observed that the longest edge (3.28 Å) is almost perpendicular (angle 87.2°) to the screw axis, whereas the shortest edge (2.94 Å) is almost parallel (angle 4.7°) to this axis. The same type of deformation is also found in CuDnPMTC, where the longest and shortest edges (3.06 and 2.70 Å) make similar angles with the screw axis (87.0° and 3.3°). As has been mentioned earlier the hexameric molecules of the copper and silver compounds are packed in a similar way.

The central octahedron in AgDnPDTC is, however, less regular than in AgDnPMTC. In this compound, the average polar edge is 3.77 Å, whereas the average equatorial edge is 3.02 Å, *i.e.* almost the same value as that found in AgDnPMTC (3.04 Å). The difference between the lengths of the polar and equatorial edges is accordingly striking in this case. In relation to AgDnPMTC, the octahedron of AgDnPDTC gives the impression of being compressed in a direction perpendicular to the polar faces while retaining the same equatorial

edges. Thus, the distance between the planes of the polar faces is 2.10 Å in AgDnPDTC, and 2.42 Å in AgDnPMTc. The difference in the dimensions of the monothiocarbamate and the dithiocarbamate ligands is also of relevance in this context. In AgDnPDTC, the distance between the two sulphur atoms in the ligand has the average value 3.00 Å, whereas the corresponding sulphur–oxygen distance is 2.64 Å in AgDnPMTc, and 2.65 Å in CuDnPMTc. These and certain other factors influencing the metal–metal distances will be discussed in a later section.

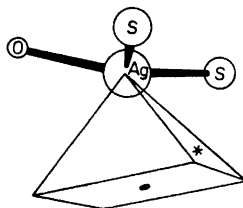


Fig. 5. Perspective illustration of the coordination around the silver atom. The four adjacent silver atoms in the octahedron are included. A dot indicates the centre of the molecule. The visible polar face is marked by a star.

The coordination. As shown in Fig. 5, each silver atom in AgDnPMTc coordinates two sulphur atoms and one oxygen atom. The threefold coordination around the metal atom is not planar, the average distance from the silver atom

Table 8. Distances and angles of coordination.

Atoms	a. Distances in Ångström units				
	Dist.	σ	Atoms	Dist.	σ
Ag _I – S _{II}	2.46	0.01	Ag _{III} – S _I	2.45	0.01
Ag _I – S _{III}	2.49	0.01	Ag _{III} – S _{II}	2.44	0.01
Ag _I – O _I	2.34	0.03	Ag _{III} – O _{III}	2.36	0.04
Ag _{II} – S _{III}	2.47	0.01			
Ag _{II} – S _I	2.47	0.01			
Ag _{II} – O _{II}	2.38	0.04			
Atoms	b. Angles in degrees				
	Angle	σ	Atoms	Angle	σ
S _{II} – Ag _I – S _{III}	126.6	0.4	S _I – Ag _{III} – S _{II}	125.5	0.5
S _{II} – Ag _I – O _I	109.5	0.9	S _I – Ag _{III} – O _{III}	111.4	0.9
S _{III} – Ag _I – O _I	113.1	0.9	S _{II} – Ag _{III} – O _{III}	115.9	0.9
S _{III} – Ag _{II} – S _I	124.7	0.5	Ag _I – S _{II} – Ag _{III}	78.5	0.4
S _{III} – Ag _{II} – O _{II}	116.9	0.9	Ag _{II} – S _{III} – Ag _I	78.5	0.4
S _I – Ag _{II} – O _{II}	111.5	0.9	Ag _{III} – S _I – Ag _{II}	83.5	0.4

to the plane through the coordinated atoms being 0.40 Å (Ag_I : 0.46, Ag_{II} : 0.37, Ag_{III} : 0.38). The silver atom is always found on the same side of this plane as the centre of the molecule and the four adjacent silver atoms.

The angles of coordination are given in Table 8. Even if the average sulphur–silver–sulphur angle (126°) is somewhat larger than the average sulphur–silver–oxygen angle (113°), the coordination is still very nearly regular. The distances of coordination are also given in Table 8. It can be seen from this table, that the deviations from the mean of the silver–sulphur (2.46 Å) and the silver–oxygen (2.36 Å) distances are less than 0.02 Å. The variation observed is thus less than 1 % of the average values. The constancy of these values shows that the coordination distances are not influenced by the packing conditions to the same degree as the distances between the metal atoms.

The average silver–sulphur distance in AgDnPMTC (2.46 Å) is close to the corresponding Ag– S_B (2.51 Å) and Ag– S_A (2.35 Å) distances in AgDnPDTTC.² The silver–sulphur distances in AgDnPMTC also agree well with the distances reported in a large number of other compounds, for instance silver isocyanate, AgSCN (2.43 Å),²² and bis(thiourea)silver chloride, Ag[SC(NH₂)₂]₂Cl (2.43–2.59 Å).²⁰

The silver–oxygen distances are 2.34, 2.36, and 2.38 Å in AgDnPMTC. In other compounds the corresponding distances between oxygen and univalent silver atoms show great variation. Short distances have been found in silver oxide, Ag₂O (2.05 Å),²³ and in sodium argentate, Na₃AgO₂ (2.09 Å).²⁴ In these two compounds, the silver coordination is twofold. In silver tetraborate, Ag₂O·4B₂O₃, the shortest distance is 2.23 Å, and the longest 3.02 Å.²⁵ In silver permanganate, AgMnO₄, the Ag–O distances are within the range 2.33–2.67 Å,²⁶ and in silver polyphosphate, (AgPO₃)_x, the Ag–O distances around the five coordinate silver atoms are between 2.37 and 2.69 Å.²¹

A COMPARISON BETWEEN SOME THIOCARBAMATE LOW POLYMERS

The dithiocarbamates and monothiocarbamates of the coinage metals, Cu, Ag, and Au, studied by this group, occur as low polymers, (AX)_n, where $n = 2, 4, 6$. Some characteristic features of the compounds to be discussed are presented in Table 9. The dimer is represented by AuDnPDTTC, the tetramer by CuDEDTC, and the hexamers by CuDnPMTC, AgDnPMTC, AgDnPDTTC, and AgDEDTC. The metal atoms form a central pair in the dimer, a central tetrahedron in the tetramer and a central octahedron in three of the hexamers. In AgDEDTC, the metal atoms form a doubly bent Ag₆ chain. The metal–metal distances are generally comparable with those in the corresponding metal, but in the dimeric gold compound they are appreciably shorter. The metal coordination is twofold in the dimer and threefold in all the other compounds.

The complexes containing central metal polyhedra (tetrahedra, octahedra) have important features in common, and will be discussed in detail. The compounds AuDnPDTTC and AgDEDTC, however, show marked differences from the others.

Table 9. Characteristic features of some copper and silver dithiocarbamates and monothiocarbamates.

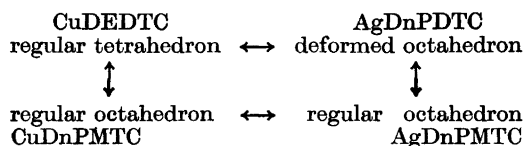
Notation	Compound Formula	Polymerity	Metal coordination	Metal arrangement	Ref.
AuDnPDTC	$[(C_2H_5)_2NCS_2Au]_2$	Dimeric	Twofold	Pair	3
CuDEDTC	$[(C_2H_5)_2NCS_2Cu]_4$	Tetrameric	Threefold	Regular tetrahedron	6
CuDnPMTC	$[(C_3H_7)_2NCOSCu]_6$	Hexameric	Threefold	Regular octahedron	4
AgDnPMTC	$[(C_3H_7)_2NCOSAg]_6$	Hexameric	Threefold	Regular octahedron	5
AgDnPDTC	$[(C_3H_7)_2NCS_2Ag]_6$	Hexameric	Threefold	Deformed octahedron	5
AgDEDTC	$[(C_2H_5)_2NCS_2Ag]_6$	Hexameric	Threefold	Doubly bent chain	3

The appearance of the gold compound as a dimer is probably due to a tendency for the gold atoms to take up twofold coordination. The short metal-metal distance (2.76 Å), however, also seems to indicate the existence of bonding interactions between the metal atoms.

The hexameric molecule of AgDEDTC, in which the metal atoms form a doubly bent chain, is different from the other hexamers. In this compound, two of the silver atoms are close (2.99 Å) to sulphur atoms in neighbouring molecules in the crystal, so there is therefore considerable interaction between the molecules, which probably causes a deformation of the arrangement. In the other hexameric compounds, the forces acting between the molecules are of van der Waals type only. These compounds are thus readily dissolved in organic solvents, whereas AgDEDTC is only sparingly soluble. The larger interactions between the molecules in this compound are explained by the smaller space required for the ethyl than for the propyl groups. This tends to make the ligand shield around the active core of the molecules less efficient. The diethyldithiocarbamate ligands form isolated low polymers with copper in the compound CuDEDTC, and this compound is readily soluble in organic solvents. This is, however, not surprising, considering the smaller size of the copper compared to the silver atoms. In Cu(I) dimethyldithiocarbamate, the screening effect of the smaller ligands is not so efficient, and accordingly, this compound has low solubility in all common solvents.⁷

Complexes containing central metal polyhedra. The compounds containing central metal polyhedra are CuDEDTC, CuDnPMTC, AgDnPDTC, and AgDnPMTC. In these complexes, the ligands are attached in the same way to the triangular faces of the polyhedra, with one of the active atoms (S) linked to two metal atoms, and the other (S or O) linked to one metal atom. Each ligand X is thus linked to three metal atoms A, and each metal atom to three ligands. The similarities in metal ligand linkage and metal coordination in these compounds make a comparison of certain details of their molecular and crystal structures of particular interest. The fundamental features of the four compounds are seen in Table 9. The characteristics of the metal arrangements

are presented in the following scheme, where a step from one corner to the next corresponds to a change in metal atom or in ligand:



Of the compounds shown, one is tetrameric, whereas the other three are hexameric. Changes from the tetrameric arrangement in the upper left hand corner to hexameric arrangements are noticed when the radius of the metal atom is increased (Cu→Ag) or when the ligand "bite" is decreased (dithiocarbamate→monothiocarbamate). It can also be noticed that the central metal polyhedron is almost regular in CuDEDTC, CuDnPMTTC, and AgDnPMTTC, whereas it is markedly deformed in AgDnPDTTC.

The molecular structures of these compounds are influenced by a number of factors, among them the metal coordination, the coordination around the active atoms in the ligands, the metal-metal distances, and the dimensions of the ligands. Many of these factors are interrelated *via* the linkage and the molecular geometry, as has been shown by Hesse,^{5,6} and the bonding conditions in the structures thus represent a compromise between the different governing factors. A complete analysis of these factors is obviously extremely difficult and beyond the scope of this paper, but an attempt will be made to relate the observed difference in structure to the different characteristics of the metal atoms and the ligands. A brief discussion of some aspects on the packing of the molecules in the crystal will also be made.

Metal-metal interactions. Short distances between metal atoms occur in all four compounds. A comparison of intermetallic distances in some Ag(I) compounds was given in Table 7. Although considerably shorter distances than those in AgDnPMTTC and AgDnPDTTC have been reported, the shortest distances in these two compounds are so close to the interatomic distance in metallic silver, 2.89 Å,¹⁴ that interaction between the metal atoms cannot immediately be ruled out. There are in fact some compounds with metal-metal bonds, where the interatomic distances exceed those of the corresponding metallic phases by proportionately larger amounts than those in the thiocarbamates of silver. In Os₃(CO)₁₂^{13,2} and Ru₃(CO)₁₂^{13,23} the trinuclear complexes are maintained by metal-metal bonds only, since there are no bridging groups, and the distances between the metal atoms in these compounds are 2.88 and 2.85 Å, as compared to the distances in metallic osmium, 2.68 Å,¹⁴ and ruthenium, 2.65 Å.¹⁴ In the linked structures of AgDnPDTTC and AgDnPMTTC, it is of course more difficult to ascertain whether the interaction between the metal atoms makes an important contribution to the structure. In the recently published structure of tetrabutylammonium tetraiodotriargentate,¹⁹ (C₄H₉)₄NAg₃I₄, one set of silver-silver distances is 3.06 Å, and another 3.13 Å. The authors consider that an interpretation of these lengths is "neither simple, nor certain".

In CuDnPMTTC, the average length of the shortest set of metal-metal distances, 2.79 Å, exceeds that of the metallic phase, 2.56 Å,¹⁴ by 9%, as

compared to 3 % in the two silver compounds. Important metal-metal interaction is thus less likely in the copper than in the silver compounds. As these three compounds are very similar, it is then reasonable to deduce that metal-metal interactions are of little importance in determining the fundamental structural features.

Evidence against strong metal-metal interaction is also obtained from an investigation of the variation of those interatomic distances which are equivalent with respect to linkage. Bonds between the metal atoms would obviously tend to make the metal-metal distances stable against external forces. It has, however, already been mentioned that these distances in AgDnPMTc appear to be more affected by the packing conditions than the coordination distances. The same observation holds for CuDnPMTc, and to a much greater extent for AgDnPDTC. In this compound, metal-metal interaction is definitely excluded, at least along the polar edges, as can be seen from the large intermetallic distances along these edges (average 3.77 Å).

It is then probable that the metal-metal distances are determined by factors other than metal-metal bond interactions. These distances could, for instance, be determined by the distances and angles of coordination and by the geometry of the central part of the ligands.

Coordination around the metal atom. The coordination around the metal atom is threefold in all four compounds studied. As has been pointed out earlier, there is little variation in the distances of coordination. The three angles of coordination are of two kinds: those containing two two-coordinated atoms (S), and those containing one two-coordinated atom (S), and one one-coordinated atom (S or O). The average value of these two kinds of angles are 100° and 127° in AgDnPDTC, 126° and 113° in AgDnPMTc, 121° and 114° in CuDnPMTc, and 121° and 119° in CuDEDTC. No general trend in the two groups of angles can be discerned and there also occur pronounced variations within the sets, represented by the average values. It thus appears that the angles of metal coordination do not have a large determining effect on the molecular geometry.

The coordination is not planar in any of the compounds, the average deviation of the metal atoms from the planes through the coordinated atoms being 0.34 Å in AgDnPDTC, 0.40 Å in AgDnPMTc and CuDnPMTc, and 0.14 Å in CuDEDTC. In all four cases, the metal atom is situated inside the plane of the coordinated atoms, *i.e.* on the same side of the plane as the centre of the molecule. An arrangement with the metal atoms situated outside the coordinated atoms is considered unlikely, as the metal atoms would then be readily accessible for further coordination, leading to interaction between the molecules. Such interaction would probably cause the molecule to be less stable and bring about a complete rearrangement of the structure.

In the tetrameric CuDEDTC, the metal atom is closer to the plane of the coordinated atoms than in any of the other compounds. It is evident that a larger metal atom or a shorter ligand bite in a similar tetramer would place the metal atom closer to or outside this plane. Such an unfavourable arrangement with the metal atom outside the coordinated atoms was found in a tetrameric model of AgDnPMTc with the same linkage as in CuDEDTC. For this reason, tetramers of the compounds containing silver atoms or mono-

thiocarbamate ligands would probably be unstable. This provides a reasonable explanation for these compounds appearing as hexamers. Thus, the relation between the size of the metal atoms and the ligand bite probably has important influence on the linkage and the polymerity of these compounds.

Coordination around the sulphur and oxygen atoms. The angles of coordination around the two-coordinated sulphur atoms are of two types: the metal-sulphur-metal angles and the metal-sulphur-carbon angles. The metal-sulphur-metal angles exhibit different values, 72° in CuDEDTC, 80° in AgDnPMTc, 84° in CuDnPMTc, and 97° in AgDnPDTC. In bis(thiourea)silver chloride²⁰ two values for the corresponding silver-sulphur-silver angles are found, 133.4° and 77.3° . Evidently, angles of this type can take different values in different structures.

In contrast, the other angles around the two-coordinated sulphur atom, the metal-sulphur-carbon angles, only appear to vary slightly, the average values being 109° in CuDEDTC, and 105° in CuDnPMTc and AgDnPDTC. Similar regularity is also found in the corresponding angles around the one-coordinated sulphur atom in the dithiocarbamate compounds, the average value being 102° in both AgDnPDTC and CuDEDTC. The metal-oxygen-carbon angles in CuDnPMTc have the average value 117° . The values of these angles for AgDnPMTc are not included here because of the low accuracy obtained for the carbon atoms in this case, but it is reasonable to assume that these angles would be close to those found in CuDnPMTc.

Using these angles, the observed coordination distances, and the observed distances and angles in the ligands, it is seen that two metal atoms connected by a sulphur-carbon-sulphur or a sulphur-carbon-oxygen bridge cannot be in the same plane as the three atoms of the ligand. Such a planar arrangement would involve far too short intermetallic distances, *e.g.* about 1.9 \AA in the silver dipropyldithiocarbamate compound. The intermetallic distances increase if one of the metal atoms is moved out of the plane. This happens in the hexameric compounds, where the equatorial edges are bridged in this way.

Let us take a reasonable model for the central part of a hexameric molecule as consisting of the metal, sulphur (oxygen), and inner carbon atoms. The angles and distances in the ligands are taken as those found in the structures. This idealized model is given the symmetry $\bar{3}$. One of the three metal atoms connected to a ligand is placed in the plane of the three ligand atoms, and the other two metal atoms are situated symmetrically with respect to this plane. With this configuration and with the coordination distances and the metal-sulphur (oxygen)-carbon angles fixed at their average observed values, one degree of freedom remains in the model. The other parameters of interest, the coordination angles around the metal atoms, the lengths of the polar edges, the lengths of the equatorial edges and the metal-sulphur-metal angles are then interdependent, so that a relationship between them can be obtained for each compound. If, for instance, the equatorial edge is given a certain value, then all other parameters will be determined. With this simple model of the linkage in the hexameric molecules, both the intermetallic distances and the angles of coordination around the metal atom can be related to essential features in the ligands.

Although the actual structures are clearly deformed by packing effects, the observed values in AgDnPDTC and AgDnPMTC agree well with this model. As the ligands are different in these two compounds, the relationships between the polar and the equatorial edges are different too. The equatorial edges in the octahedra are very similar, average values 3.02 Å in AgDnPDTC, and 3.04 Å in AgDnPMTC. This is probably because a closer approach of the metal atoms would lead to strong repulsion. In the model, the polar edges are then considerably larger in AgDnPDTC than in AgDnPMTC, and this is also found in the crystal structure, 3.77 Å *vs.* 3.17 Å. The observed differences in the metal–sulphur–metal and the sulphur–metal–sulphur angles also agree with the model.

Some aspects of molecular shape. Even if differences exist in shape, the molecules of the three hexameric compounds have the fundamental features in common. It may therefore be surprising to note that these very similar molecules pack in two different ways in their crystal structures. The molecules of AgDnPMTC and CuDnPMTC are related by screw axes and glide planes according to the monoclinic space group $P2_1/a$. In the crystal structure of AgDnPDTC, however, the molecules are related by translation and centres

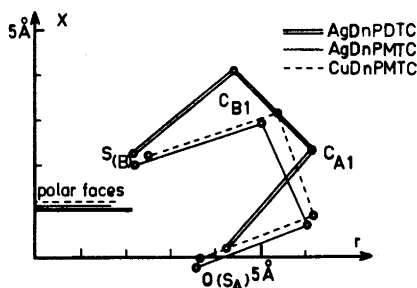


Fig. 6. Some characteristics of the shapes of the hexameric molecules in AgDnPMTC, AgDnPDTC, and CuDnPMTC. The drawing shows the coordinated sulphur and oxygen atoms, and the first carbon atoms in the two propyl chains. The polar faces are also indicated. The X -axis corresponds to the X -axis of Fig. 3. The distances of the atoms from this axis are shown on the r -axis.

of symmetry only according to the triclinic space group $P\bar{1}$. These differences in packing can be related to the differences in molecular shape. Fig. 6 shows a projection of the molecules in a direction perpendicular to the approximate threefold axis of the three molecules (X -axis, *cf.* Table 5). The radial distance from this axis is shown on the r -axis, and the centre of the molecules are placed at the origin. The positions indicated for the sulphur, oxygen, and the first carbon atoms in the two propyl chains are the average positions of these atoms in the three ligands. These atoms show clearly the position and orientation of the ligand. It is seen that the shapes of the AgDnPMTC and CuDnPMTC molecules are very similar. In the AgDnPDTC molecule, however, the ligands are more inclined towards the X -axis. Thus, there appears to be less space available in AgDnPDTC close to this axis and close to the polar face for the

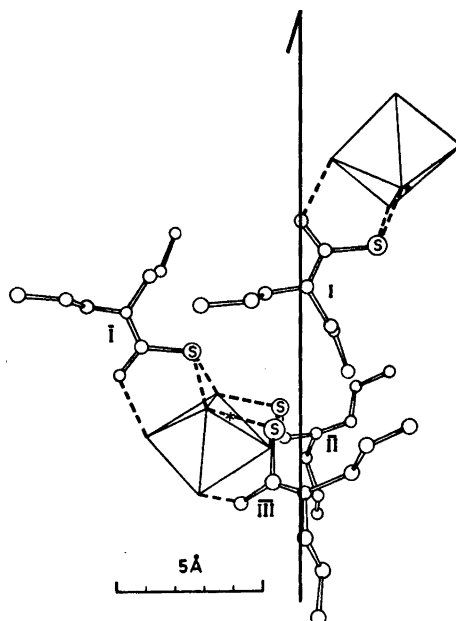


Fig. 7. Detail of the packing arrangement in AgDnPMTC. The lower silver octahedron shown has its centre at $(0,0,0)$, and the upper one at $(\frac{1}{2}, \frac{1}{2}, 0)$ (cf. Fig. 2). The two octahedra are related by the screw axis indicated. The two visible polar faces are marked by stars. One ligand is drawn for the upper molecule, and three for the lower one. The ligand I of the upper molecule is situated in the bowl formed by the three ligands I, II, and III, which point upwards from the lower molecule (cf. Fig. 3).

accommodation of atoms from other molecules. It can be seen in Fig. 7 that the corresponding space in AgDnPMTC accommodates the propyl chains of a ligand from a second molecule related to the first by a screw axis. In the crystal structure of AgDnPDTC, there is no such fit between the molecules.

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