The Crystal and Molecular Structure of the Gold(I)

Dipropyldithiocarbamate Dimer

ROLF HESSE and PER JENNISCHE

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

The crystal structure of gold(I) dipropyldithiocarbamate, $(C_3H_7)_2NCS_2Au$, has been determined from three-dimensional X-ray data. The crystals are tetragonal, space group $P\bar{4}b2$. Unit cell parameters are $a = 13.194$ Å, $c = 6.162$ Å. The structure consists of isolated $[(C_3H_7)_2NCS_2Au]_2$ dimers. There are two dimeric molecules in the unit cell. The gold atoms form a central pair in the molecule. The gold-gold distance (2.76 Å) is shorter than that in the metallic phase of gold. Each gold atom is linked to two sulphur atoms in two different ligands by linear coordination. The molecules are packed so as to form linear gold chains with alternating distances 2.76 Å and 3.40 Å.

The short metal-metal distance in the molecule is discussed with reference to other elements in the molecule. The carbon-sulphur-metal angle appears to be of particular importance for the geometry of the molecule.

The determination of the crystal structure of gold(I) dipropyldithiocarbamate forms part of a series of crystal studies on $(AX)_n$ compounds carried out by the present research group. A represents an alkali metal, a univalent coinage metal or a univalent thallium atom; X is a dialkyldithiocarbamate, a dialkyl-monothiocarbamate, 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-type [2,3] structures or low polymers.[4-7] There are also marginal cases.[8] In the crystal structures consisting of isolated low polymeric units cases of n equal to 2, 4, and 6 have been encountered. Among the compounds studied gold(I) dipropyldithiocarbamate is the first representative of a structure being built from isolated dimeric units $(AX)_2$. The corresponding thallium compound [2] also forms dimeric molecules in solution [9] but the crystal structure is a high polymer of the chain type.

The dimer in gold(I) dipropyldithiocarbamate is of special interest because of the short gold-gold distance (2.76 Å) appearing in the molecule. This distance will be related to other elements in the molecule by the use of a simple geometric model.

EXPERIMENTAL

Crystals of $[(C_3H_7)_2NCS_2Au]_2$ were supplied by Åkerström who had prepared them according to his published method.[10] The crystals were obtained from pyridine as yellow needles with the needle 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 elemental silicon as a calibrant ($a = 5.4305$ Å [11]). Unit cell and symmetry data are given in Table 1.

Table 1. Unit cell and symmetry data.

Formula unit: $(C_3H_7)_2NCS_2Au$.
Crystal system: tetragonal.
Unit cell parameters: $a = 13.194$ Å ± 0.005; $c = 6.162$ Å ± 0.003.
Volume of unit cell: 1073 Å^3.
Density (measured): 2.28 g cm^{-3}.
Number of formula units per unit cell: 4.
Density (calculated): 2.31 g cm^{-3}.
Diffraction symmetry: $4/mmm$.
Systematic absences: $h0l$ for $h = 2n + 1$; $0kl$ for $k = 2n + 1$.
Space group: $P\bar{4}b2$.
Coordinates of equivalent positions:

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

The X-ray reflexions were recorded on equi-inclination Weissenberg photographs using $CuK\alpha$ radiation. The multiple film technique was employed using six films. The intensities were estimated visually using calibrated intensity scales. Three sets of data were collected from three different crystals as shown in Table 2. Corrections were made

Table 2. Crystals.

Data set	Crystal size (mm)	Layers	Measured reflexions	Independent reflexions
I	$0.103 \times 0.054 \times 0.042$	$hk0$	209	74
		$hk1$	175	57
		$hk2$	239	62
		$hk3$	150	47
		$hk4$	173	55
II	$0.275 \times 0.021 \times 0.013$	$h0l$	92	54
		$h1l$	76	42
		$h2l$	105	65
		$h3l$	68	40
		$h4l$	74	42
		$h5l$	61	32
		$h6l$	43	26
III	$0.190 \times 0.013 \times 0.011$	$hk0$	80	44
		$hk1$	66	33
		$hk2$	131	67
		$hk3$	51	28
		$hk4$	32	18

for Lorentz and polarization effects but not for extinction and absorption. Preliminary interlayer scale factors for data sets I and II were determined from the common reflexions in set I and the first four layers in set II. Improved scale factors for the entire material in set II were determined from the tetragonal Laue-symmetry. Data set III was introduced at a later stage. Average values of the intensities from the three sets were calculated for the 264 independent reflexions used in the computation. The high diffraction symmetry, $4/mmm$, provides a check on the measurements of the intensities. Most of the intensities used are thus average values of two or three independent measurements in each data set.

DETERMINATION OF THE ATOMIC POSITIONS

The observed diffraction symmetry and the systematic absences (Table 1) suggest the space group to be $P4bm$, $P4/mbm$ or $P\bar{4}b2$. Of these the first two must be discarded for geometric reasons. In the remaining space group, $P\bar{4}b2$, the general position is eight-fold. As there are four formula units in the cell, the gold atoms must then occupy special positions. Of the four sets of four-fold positions in this space group only two, $4(e)$ and $4(f)$, are consistent with the maxima in the Patterson synthesis. One of these, $4(e)$, can be discarded for geometric reasons. In the remaining set of special positions, $4(f)$, the x and y coordinates of the gold atom are fixed. The z coordinate of the gold atom was determined from an investigation of the intensity distribution in the layers $hk1$ to $hk7$. Approximate positions for the remaining atoms, except the hydrogen atoms, were then obtained from three-dimensional difference syntheses in combination with sterical considerations. No attempt was made to locate the hydrogen atoms.

The positions of all non-hydrogen atoms were refined by three-dimensional Fourier syntheses using the backshift technique. The atomic positions and isotropic temperature factors were refined by the method of least squares. 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.,[12] $\omega=1/(a+|F_o|+c|F_c|^2)$. The constants used in the final cycles were $a=2.0$, $c=0.01$. Atomic scattering factors for the elements were obtained from the International Tables, Vol. III,[13] as follows: gold (Table 3.3.1B, p. 212); sulphur, nitrogen and carbon (Table 3.3.1A, pp. 202 – 203). The real part of the dispersion corrections for gold and sulphur were applied.[14] The least squares refinement was 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 13.8 %. The atomic parameters from the last cycle of the refinement are shown in Table 3. When corrections for anomalous scattering of gold and sulphur were applied and anisotropic temperature factors for the gold and sulphur atoms were introduced in the refinement the index R decreased to 10.5 %. The shifts on the atomic coordinates were insignificant. The distances and angles in the propyl chains for the positions obtained from the least squares refinement deviated somewhat from the expected values. The three carbon atoms were therefore moved within the electron density maxima so as to obtain more reasonable values. The largest correction was 0.2 Å. The corrected positions are presented in Table 3 with the least squares parameters enclosed in brackets. The distances and angles in the molecule are shown in Table 4.

Table 3. Atomic parameters with standard deviations indicating the error in the last digit. Notation, see Fig. 3. The coordinates for the propyl carbon atoms presented without brackets correspond to the corrected positions.

Atom	x	y	z	B
Au	$\frac{1}{2}$	0	0.2239(6)	5.5(1)
S	0.348(1)	0.081(1)	0.223(4)	5.7(3)
C_1	0.344(4)	0.156(4)	0	4(1)
N	0.273(4)	0.227(4)	0	6(2)
C_3	0.200	0.248	0.180	
	[0.190(6)	0.246(6)	0.19(2)	7(2)]
C_5	0.106	0.180	0.153	
	[0.112(7)	0.177(7)	0.12(2)	9(3)]
C_7	0.043	0.184	0.360	
	[0.046(8)	0.192(8)	0.39(2)	9(3)]

The high symmetry assumed for the structure is verified by the diffraction data. When all the atoms were located a check was performed on the symmetry by a least squares refinement using lower symmetry. No significant deviation from the tetragonal symmetry was observed. Any deviation from the assumed symmetry is thus likely to be small. The diffuse maxima obtained for the carbon atoms in the propyl chains are the only indications in favour of a lower symmetry. The broad maxima may thus be superpositions of close but not identical maxima. However, a more probable explanation is provided by disorder which is likely to occur in this compound as in several others studied by the group.

Table 4. Distances and angles in the dimeric molecule with standard deviations indicating the error in the last digit. Corrected positions have been used for the carbon atoms in the propyl chain.

a. Distances in Å		b. Angles in degrees	
Atoms	Distances	Atoms	Distances
Au – Au	2.76(1)	S – Au – S	180(1)
Au – S	2.28(2)	Au – S – C_1	108(2)
S – C_1	1.70(2)	S – C_1 – N	116(2)
C_1 – N	1.32(5)	S – C_1 – S	128(3)
N – C_3	1.50	C_1 – N – C_3	126
C_3 – C_5	1.54	C_3 – N – C_2	108
C_5 – C_7	1.52	N – C_3 – C_5	109
S⋯S	3.05	C_3 – C_5 – C_7	109

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

General features. The structure is built from discrete dimeric molecules $[(C_3H_7)_2NCS_2Au]_2$. There are two such molecules in the unit cell as is shown in Fig. 1 which is a projection on the xy plane. The tetragonal symmetry of
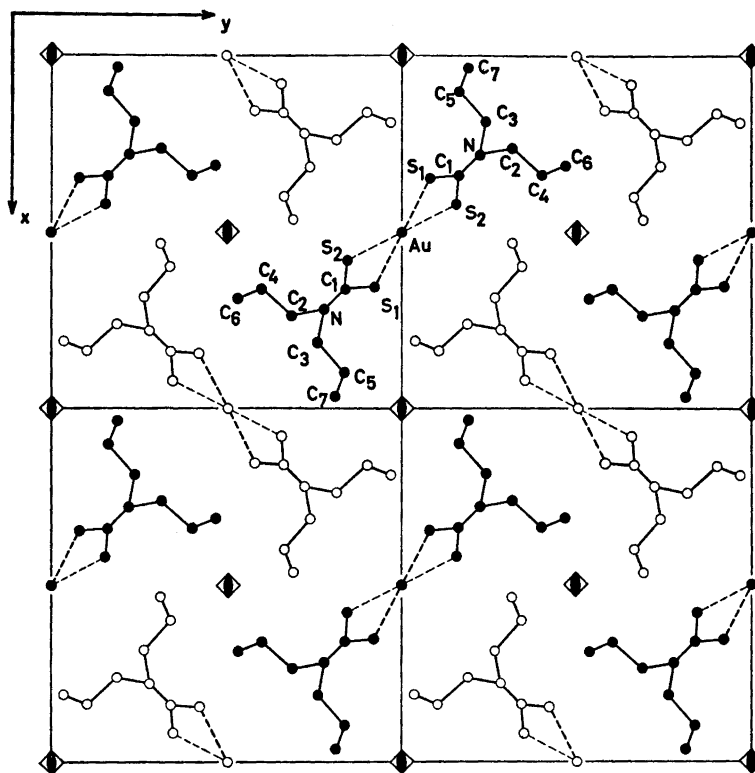
Fig. 1. xy-Projection of four unit cells of the structure of gold dipropyldithiocarbamate.

the arrangement is immediately seen from the figure. The gold atoms occupy four-fold positions, 4(f), on two-fold axes parallel to **c**. The nitrogen and inner carbon atoms similarly occupy four-fold positions, 4(g), on two-fold axes parallel to **a** + **b**. Fig. 2 is the corresponding yz projection. It is seen from the two figures that the dimeric molecules are stacked on top of each other forming chains in the **c** direction. Within these chains the gold atoms form linear strings with the alternating interatomic distances 2.76 Å and 3.40 Å. The interactions between the chains are of van der Waals type as can be observed from the intermolecular distances listed in Table 5. The shortest distance be-

Table 5. Intermolecular distances shorter than 4 Å. The relation of the atoms in the second column to those given in Table 3 (coordinates x, y, z) is shown.

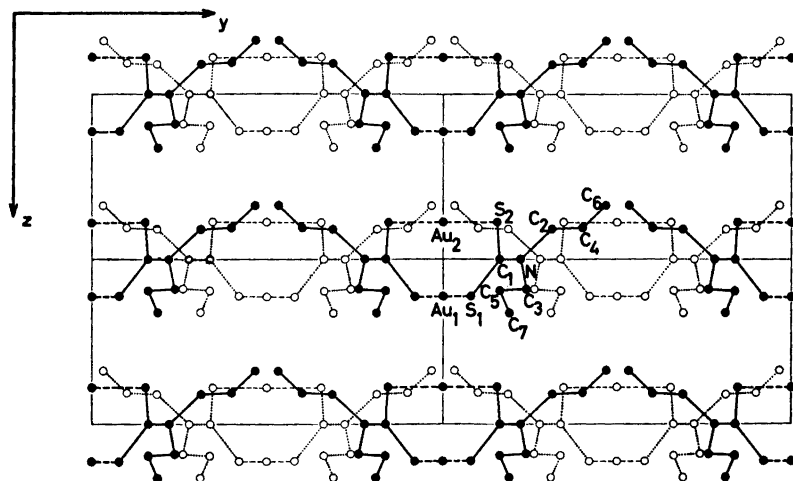| Atoms			Distance (Å)
Au	Au	$\frac{1}{2}-y$, $\frac{1}{2}-x$, $1-z$	3.40
S	S	$\frac{1}{2}-y$, $\frac{1}{2}-x$, $1-z$	3.67
S	C_7	y, $\bar{x}$, $1-z$	3.74
C_7	C_7	y, $\bar{x}$, $1-z$	3.93

Fig. 2. yz-Projection of four unit cells of the structure of gold dipropyldithiocarbamate.

tween atoms in different chains is the sulphur-carbon distance 3.74 Å. Within the chains the atoms in different dimeric units approach each other somewhat more closely, the shortest distance of this type being the gold-gold distance 3.40 Å.

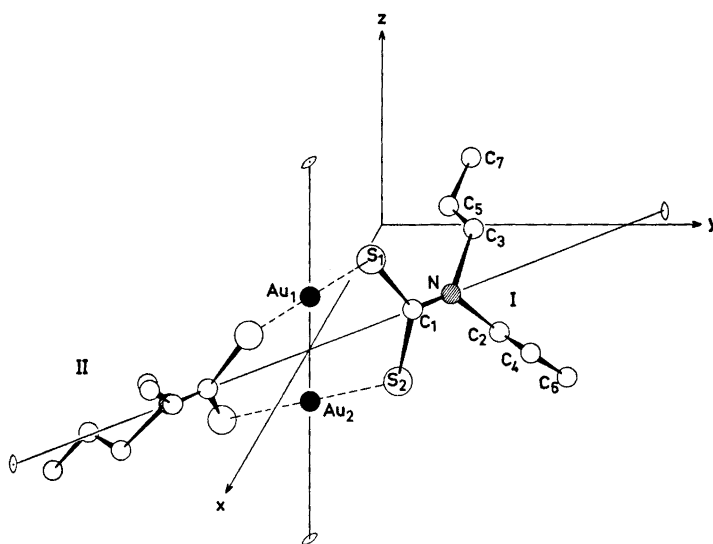The dimer. A diagram of the dimeric molecule is shown in Fig. 3. The gold

Fig. 3. The dimeric molecule of gold dipropyldithiocarbamate.

atoms form a central pair with intermetallic distance 2.76 Å. Each gold atom coordinates two sulphur atoms from different ligands. By this arrangement the gold atoms achieve the linear coordination usually found in Au(I) compounds.[15] The molecule is highly symmetric as one two-fold axis passes through the two gold atoms and another through the two carbon and nitrogen atoms. The S_2CNC_2 part of the ligand is almost planar, the SCS plane making the angle 5° with the CNC plane. The planar parts of the two ligands are inclined about 50° with respect to each other so that the molecule acquires the shape of a propeller with the gold pair as the axis. As can be seen from Figs. 1 and 2 there is an equal number of left-handed (open circles) and right-handed (filled circles) molecules in the structure.

The coordination. The coordination is linear well within the experimental accuracy as shown in Table 4. The distance of coordination, Au−S, is 2.28 Å. The distance to the two other sulphur atoms in the molecule is 3.57 Å and no interaction is likely at this large distance. A covalent radius of 1.33 Å for linearly coordinated gold(I) has been deduced.[16] The somewhat smaller radius 1.21 Å is obtained from the Au(I)−Br distance, 2.35 Å, in bis(*N,N*-dibutyl-dithiocarbamate)-gold(III) dibromoaureate(I) [17] and the Br radius of Pauling, 1.14 Å.[18] The covalent radius of sulphur is 1.04 Å [18] and the Au−S distance of 2.28 Å is thus in the expected range. A similar gold-sulphur distance, 2.35 Å, was found for Au(III) having planar four-fold coordination in bis(*N,N*-di-butyldithiocarbamate)gold(III) dibromoaureate(I).[17]

The packing. As mentioned the molecules are arranged in the crystal so as to form linear gold chains with alternating distance 2.76 Å and 3.40 Å. Linear chains with Au−Au distances 3.26 Å between alternating Au(I) and Au(III) atoms were found in Au(III)(DMG)$_2$Au(I)Cl$_2$, HDMG = dimethylglyoxime, and weak gold-gold bonding was suggested. It was also mentioned that the contribution of the metallic bond is likely to be small and that such weak bonds can be destroyed by steric influencies.[19] Zigzag gold chains were found in phenylethynyl(isopropylamine)gold(I).[16] The gold-gold distances along the chains are 3.72 Å and the angles 153°. The chains are grouped in pairs so that the shorter distances 3.27 Å appear between the chains. The distances between the atoms in the zigzag gold chains of AuClPCl$_3$ were calculated from the published coordinates [20] and found to be 3.14 Å. The angles are 162°. The appearance of chains in these compounds and in gold(I) dipropyldithio-carbamate should probably be viewed in connection with the linear coordination of Au(I). There is no steric hindrance for a close approach of the gold atoms and the arrangements of the molecules appear to follow from simple linkage and packing principles.

An entirely different arrangement of dimeric units is found in the crystal structure of thallium(I) dipropyldithiocarbamate, $(C_3H_7)_2NCS_2Tl$.[2] The two thallium and four sulphur atoms in the dimeric molecules form a distorted octahedron with the thallium atoms occupying opposite corners. Zigzag thallium chains are formed by Tl−S bonds between neighbouring dimers. The similar dimers of thallium(I) di-isopropyldithiocarbamate [3] form chains of the same kind but with a different arrangement of the Tl−S bonds between the dimers. No evidence of corresponding Au−S interaction is found in gold(I) dipropyldithiocarbamate. This remarkable difference between the gold and

the thallium compounds is most likely caused by the different coordination requirements of the metal atoms.

A geometrical interpretation. The gold atoms in the dimeric molecule approach each other more closely (2.76 Å) than in the metallic phase of gold (2.88 Å).[21] Although it is tempting to associate this short gold-gold distance with bonding interactions, such interactions are not easily interpreted in orbital terms. Furthermore, the gold-gold distance is not an isolated feature but occurs as only one parameter among several in a complicated linked system. The different parameters (distances between atoms and bond angles) are then dependent on each other according to a relation formulated by Hesse [4,5] in the study of the tetrameric molecule $[(C_2H_5)_2NCS_2Cu]_4$. Similar dependencies occur in another linked system which is represented by the hexameric molecules silver(I) dipropyldithiocarbamate,[5] silver(I) dipropylmonothiocarbamate,[6] and copper(I) dipropylmonothiocarbamate.[7] In these compounds the metal atoms form central octahedra with metal-metal distances close to those of the corresponding metallic phases. The intermetallic distances can be related to essential features of the ligands by using a simple geometric model.[6] In the following discussion a similar relation will be derived for the dimeric molecule in gold(I) dipropyldithiocarbamate.

Let us take a reasonable model for the central part of the molecule as consisting of the two gold, the four sulphur and the two inner carbon atoms. Two perpendicular two-fold axes of symmetry are introduced, one containing the two gold atoms and the other the two carbon atoms. The model then has the same symmetry as the molecule in the crystal. The degrees of freedom of the model are reduced by fixing the distances and angles in the sulphur-carbon-sulphur group and the distances of coordination at the values obtained in the crystal structure. Finally linear coordination for the gold atoms is postulated. All these postulates in the model correspond to chemically reasonable assumptions which are in accordance with the observed features of the structure. However, the model now has only one degree of freedom so that a relationship can be established between any two or more parameters considered. The two parameters of the greatest chemical interest are the carbon-sulphur-gold angle, ν, and the gold-gold distance, p. The relationship between p and ν in the model is shown in Fig. 4. The slope $dp/d\nu$ is easily obtained from the curve
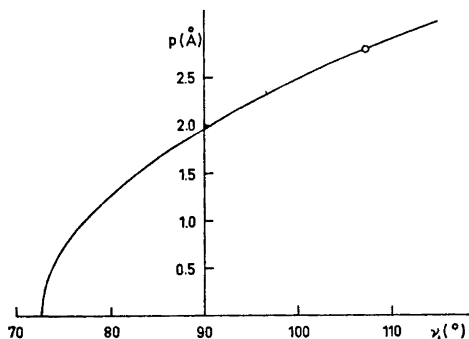

Fig. 4. The relationship between the Au – Au distance, p, and the C – S – Au angle, ν, in the model described in the text. A circle shows the values found in the molecule in the structure.

Table 6. Carbon-sulphur-metal angles in various coinage metal compounds.

Compound	Carbon-sulphur-metal angle (°)		Ref.
	Two-coordinated S	One-coordinated S	
[(C$_3$H$_7$)$_2$NCS$_2$Au]$_2$		108	—
[(C$_3$H$_7$)$_2$NCS$_2$Ag]$_6$	105 [a]	101 [a]	5
[(C$_2$H$_5$)$_2$NCS$_2$Cu]$_4$	109 [a]	102	4
[(C$_3$H$_7$)$_2$NCOSCu]$_6$	105 [a]		7
Ag[SC(NH$_2$)$_2$]$_2$Cl	106 [a]	104 [a]	22
Ag[SC(NH$_2$)NHNH$_2$]Cl	107 [a,b]		23
AgSCN		104	24
NH$_4$Ag(SCN)$_2$		110	25

[a] Average value.
[b] Calculated from published data.

and it is found to be very close to 0.04 Å/degree in the almost linear region in the vicinity of the observed value $p = 2.76$ Å. Thus, if the carbon-sulphur-gold angle in the model is changed by only ten degrees the gold-gold distance will change by as much as 0.40 Å. A tendency of the corresponding angle in the structure to assume a certain value would then probably execute a strong influence on the distance between the gold atoms. The $C-S-Au$ angle observed in the structure is 108°. In fact, the corresponding angles have smaller values in the copper and silver dithiocarbamates and monothiocarbamates as shown in Table 6. These values would thus give even shorter gold-gold distances. For comparison some other compounds with a sulphur atom attached to a carbon and a coinage metal atom are also included in the table. (Chelation compounds have not been considered because of the strain on the angles

in the rings M⟨S⟩C —.) It thus appears that the short gold-gold distance can

be related to other elements in the molecules.

Of course, interactions between different molecules in the structure may also influence the distances and angles within the molecules. However, the intermolecular distances in this compound are quite large as has been mentioned earlier (Table 5). Apart from the gold-gold distance between two dimers (3.40 Å) only three more contacts are smaller than 4.0 Å. The long intermolecular distances in this compound indicate the absence of strong interactions between the molecules in the structure.

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