

Crystal and molecular structure of bis(N,N-di-*n*-butyldithiocarbamato)gold(III) dibromoargentate(I)

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Abstract

The crystal and molecular structure of bis(N,N-di-*n*-butyldithiocarbamato)gold(III) dibromoargentate(I), $\text{Au}(\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2)_2\text{AgBr}_2$, has been determined by three-dimensional X-ray methods. The compound crystallizes in the monoclinic space group $C2/c$ with unit cell dimensions: $a = 17.39(1)$ $b = 18.65(1)$; $c = 9.199(6)$ Å; $\beta = 93.9(1)^\circ$; $Z = 4$. Intensities were collected on an automatic diffractometer. The structural parameters were refined by least-squares methods to a conventional R factor of 0.048 for 854 non-zero observed reflexions. The structure consists of $\text{Au}(\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2)_2^+$ and AgBr_2^- ions. The gold is in planar coordination with four sulphur atoms, the two crystallographically non-equivalent Au—S bond lengths being 2.357(8) and 2.324(8) Å. The silver is linearly coordinated, the Ag—Br bond lengths being 2.450(5) Å. The ionic packing in the structure differs from that in the analogous $\text{Au}(\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2)_2\text{AuBr}_2$ complex.

Introduction

In preceding papers, the crystal structures of $\text{Au}(\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2)_2\text{AuBr}_2$ (Beurskens, Blaauw, Cras & Steggerda, 1968) and of $\text{Au}(\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2)_2\text{Br}$ (Beurskens, Cras and Van der Linden, 1970) have been reported. Study of the packing in these ionic structures has been extended by the investigation of the complex $\text{Au}(\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2)_2\text{AgBr}_2$ ($=\text{Au}(\text{dtc})_2\text{AgBr}_2$), prepared by Van der Linden (1970).

Crystal data

Bis(N,N-di-*n*-butyldithiocarbamato)gold(III)dibromoargentate(I), $\text{Au}(\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2)_2\text{AgBr}_2$ ($=\text{Au}(\text{dtc})_2\text{AgBr}_2$), FW 873.41. The prismatic crystals are elongated along c . The space group, from systematic absences, is either Cc or $C2/c$ and the structure was solved assuming the latter. Unit cell dimensions are $a = 17.39(1)$, $b = 18.65(1)$, $c = 9.199(6)$ Å, $\beta = 93.9(1)^\circ$; $V = 2977(9)$ Å³. $D_m = 1.98(2)$ g cm⁻³ (floatation method), $Z = 4$, $D_x = 1.95(1)$ g cm⁻³. Nickel-filtered copper $K\alpha$ radiation, $\lambda = 1.5418$ Å, was used. The linear absorption coefficient μ is 208.8 cm⁻¹.

A crystal, cut to approximately $0.09 \times 0.09 \times 0.14$ mm³, was mounted with c coincident with the ϕ axis. The cell dimensions were obtained from θ , ϕ and χ measurements on a Nonius diffractometer for 22 reflexions in the range $10^\circ < \theta < 30^\circ$, the values with estimated standard deviations being calculated by a least-squares method.

Intensity measurements

Intensities were collected with an automatic Nonius diffractometer, using the moving counter-moving crystal method (scan speed 0.3°/min). Every 60 min a reference reflexion was measured to detect and

Table 1. Atomic parameters for $Au(dtc)_2AgBr_2$ with standard deviations. The key to atomic numbering is given in Fig. 3.

(a) All atoms except butyl carbon atoms. The expression used for the anisotropic temperature factor is: $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$									
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au	0.0000	0.0000	0.0000	0.0036(1)	0.0033(1)	0.0116(4)	-0.0001(1)	0.0001(2)	-0.0001(2)
Ag	0.0000	0.2015(2)	0.2500	0.0062(3)	0.0059(3)	0.0209(9)	0.0000	0.0010(4)	0.0000
Br	0.1321(2)	0.2023(3)	0.1730(5)	0.0066(3)	0.0081(3)	0.024(1)	-0.0021(2)	0.0009(4)	-0.0020(5)
S(1)	0.1081(4)	0.0033(7)	0.169(1)	0.0050(4)	0.0042(4)	0.014(2)	-0.0005(5)	-0.0014(7)	-0.002(1)
S(2)	0.0278(5)	-0.1197(5)	0.050(1)	0.0040(5)	0.0040(4)	0.021(2)	-0.0004(3)	-0.0010(8)	-0.001(1)
N	0.154(2)	-0.135(2)	0.245(4)	0.006(2)	0.006(2)	0.031(9)	-0.000(1)	-0.001(3)	0.003(3)
C(1)	0.107(2)	-0.091(2)	0.173(4)	0.008(3)	0.003(2)	0.006(7)	-0.001(1)	-0.002(3)	0.000(3)

(b) Butyl carbon atoms. The positional parameters are the unrefined results of a difference Fourier synthesis (see text)									
	x	y	z	B (\AA^2)		x	y	z	B (\AA^2)
C(2)	0.211	-0.097	0.344	7(1)	C(6)	0.133	-0.222	0.256	11(2)
C(3)	0.289	-0.094	0.278	9(1)	C(7)	0.175	-0.236	0.142	9(1)
C(4)	0.353	-0.064	0.394	10(1)	C(8)	0.150	-0.328	0.134	11(1)
C(5)	0.434	-0.054	0.333	8(2)	C(9)	0.083	-0.350	0.061	16(2)

correct for fluctuations in the primary beam. Of the 1633 attainable symmetry-independent reflexions (up to $\sin \theta/\lambda = 0.50 \text{ \AA}^{-1}$), 854 reflexions have been measured above background. Absorption corrections were calculated according to the Busing & Levy (1957) procedure, using $6 \times 6 \times 8$ volume components and 8 accurately located boundary planes. From calculations for some reflexions, using a $16 \times 16 \times 16$ subdivision, the average error of the absorption correction factors was found to be 2% with a maximum error of 10%.

Determination of the structure

The structure was solved by Patterson & Fourier methods. After the initial stage of the analysis, the unobserved reflexions were rejected (practically all had calculated intensities at this stage less than

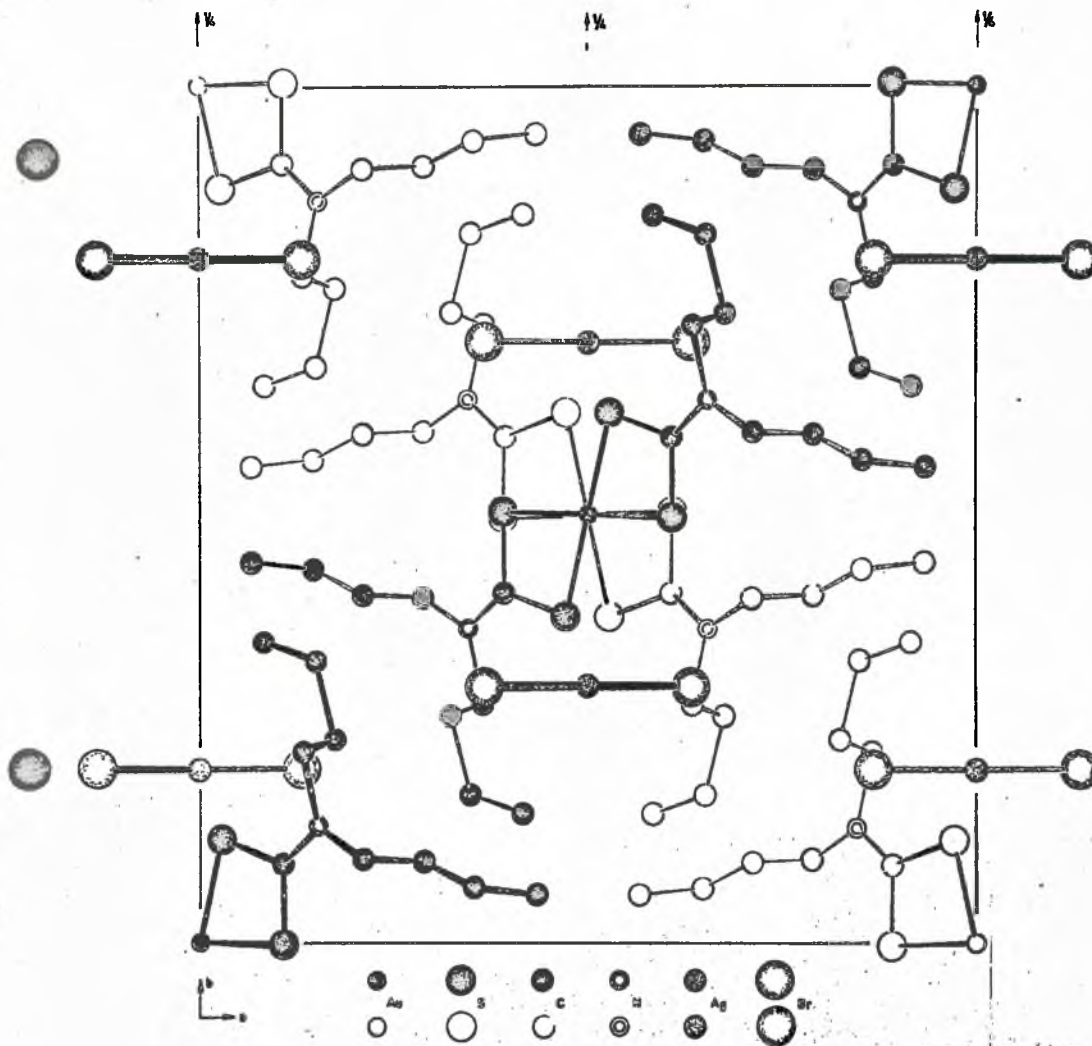


Fig. 1. Projection of $\text{Au}(\text{dte})_2\text{AgBr}_2$ along c . The white cations are situated at $z = 0$, the black cations at $z = \frac{1}{2}$. (omitted: gold atoms at $0, 0, 0$; $1, 1, 0$; $1, 0, \frac{1}{2}$ and $0, 1, \frac{1}{2}$). The twofold axes are indicated.

the minimum observable value). The positional and anisotropic vibrational parameters and the scale factor were refined by full-matrix least-squares methods. The function that was minimized was $w(|F_o| - |F_c|)^2$, the weight w for each reflexion being obtained from counting statistics. The atomic scattering factors were those of Au^+ , Ag^+ , Br^- , S, C and N corrected for the anomalous scattering component ($\Delta f'$) using data from the International Tables (1962).

After refinement of all atoms except the carbon atoms of the butyl chains, the most probable positions for these carbon atoms were sought from a difference Fourier synthesis. Refinement of these positions by least-squares methods did not affect the R value and led to improbable bond distances and angles. Also three more cycles, holding these atomic positions fixed and refining the other parameters, did not produce significant changes. According to our experience with similar structures, the failure to locate the butyl chains cannot be explained by the errors in the observed structure factors and we therefore presume that the butyl chains are disordered. The most probable

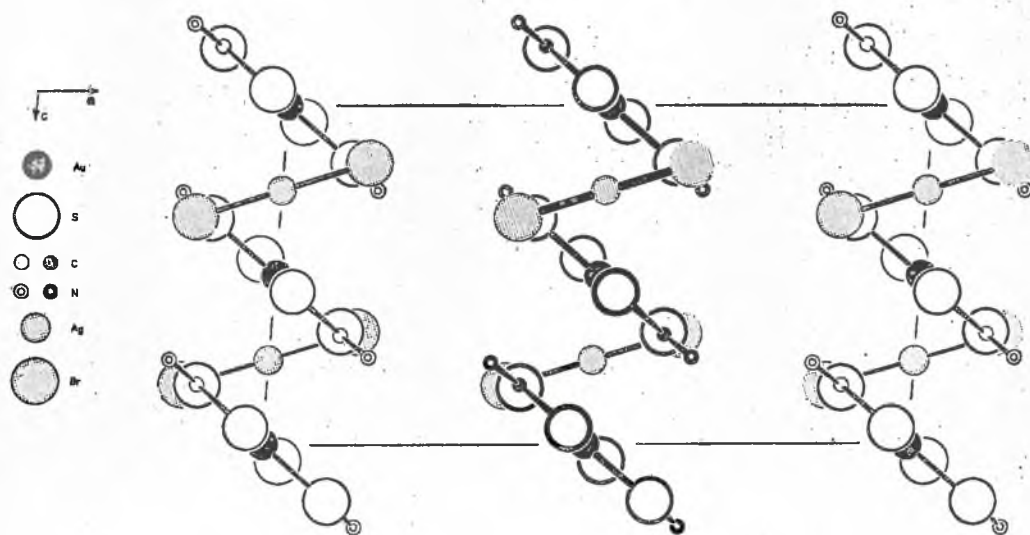


Fig. 2. Projection of $\text{Au}(\text{dte})_2\text{AgBr}_2$ along b . The butyl chains are omitted.

positions of the butyl carbon atoms, as found from the difference Fourier synthesis and listed in Table 1(b), have been included in the structure factor calculations.

The conventional R factor is 0.048. The final difference Fourier map showed some maxima of about 1 e. \AA^{-3} around the heavy atoms and 0.6 e. \AA^{-3} in the neighbourhood of the butyl chains. In view of the presumed disorder of the butyl chains and the rather large absorption corrections, we do not attach much physical significance to the temperature factor parameters given in Table 1.

Calculations were performed on an IBM 360/50 computer using programmes written by Busing, Martin & Levy (1962) and Ahmed & Pippy (1968). Programmes for cell dimensions, diffractometer setting angles and data reduction, and Fourier synthesis were written by the authors.

Description of the structure

The atomic parameters are given in Table 1. The structure is illustrated in Figs. 1 and 2, the bond distances and angles being given in Fig. 3. The table of observed and calculated structure factors is available from the authors on request.

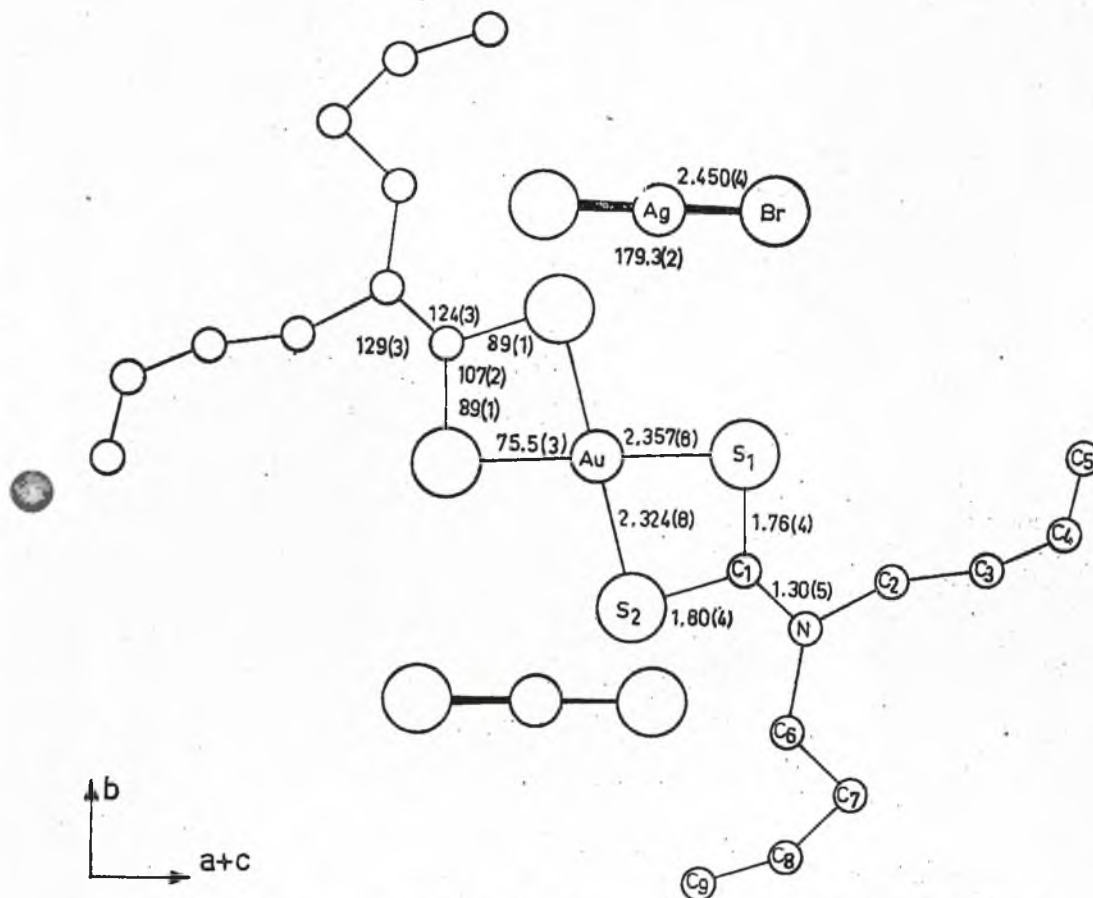


Fig. 3. Bond distances and angles. Projection perpendicular to (101). Au is situated on a centre of symmetry, Ag is situated on a twofold axis, Br is only 0.166 Å out of the plane through Au, S(1) and S(2). Standard deviations of the bond distances (Å) and angles (degrees) are given in parentheses.

The compound consists of two ionic units $\text{Au}(\text{dtc})_2^+$ and AgBr_2^- . Within the accuracy of the structure determination, the geometry of the cation in this compound is similar to that of the analogous compounds $\text{Au}(\text{dtc})_2\text{AuBr}_2$ and $\text{Au}(\text{dtc})_2\text{Br}$ (loc. cit.). The Au atom is situated on a centre of symmetry and is in planar coordination with four S atoms, the mean Au—S distance being 2.340 Å. The equation

Table 2. Interionic distances less than 4 Å

	(Å)		(Å)
Au—S(1) I	3.689(8)	S(2)—S(2) I	3.87(1)
Ag—S(2) II	3.16(1)	S(2)—N I	3.79(3)
Br—S(1)	3.74(1)	S(2)—C(1) I	3.62(4)
Br—S(2) II	3.68(1)		

The butyl carbon atoms are excluded.

Symmetry code: I: $-x, y, \frac{1}{2} - z$ II: $-x, -y, -z$

of the plane through the gold and sulphur atoms is: $0.6577x - 0.0209y - 0.7530z = 0$, with deviations from the plane of $-0.01(3)$ Å and $0.02(3)$ Å for C(1) and N, respectively. In the direction of the needle axis c , the cations are piled on top of one another, adjacent cations being related by a twofold axis. The gold atoms are $4.600(3)$ Å ($\frac{1}{2}c$) apart.

The Ag atom of the anion is situated on a twofold axis and is linearly coordinated by two Br atoms. In contrast to the analogous compounds (loc. cit.) where the anions are in the holes formed by the butyl chains, the position of the anion in the present compound is near to the sulphur of the cation. Some interionic distances are given in Table 2. The shortest contact is the Ag—S(2) distance, $3.16(1)$ Å. Br—S contacts are about 3.7 Å, the Br being only $0.166(5)$ Å out of the plane through the gold and sulphur atoms (see Fig. 2).

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National Lending Library Supplementary Publication No. 60012 contains 1 page of structure factor tables on 1 microfiche.