

Crystal and molecular structure of triphenylphosphine (*N,N*-diethyldithiocarbamato)gold(I)

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Abstract

The crystal and molecular structure of triphenylphosphine (*N,N*-diethyldithiocarbamato)gold(I), $(C_6H_5)_3PAuSSCN(C_2H_5)_2$, has been determined by three-dimensional X-ray methods. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.547(1)$, $b = 12.277(1)$, $c = 14.013(1)$ Å, $\beta = 90.81(1)^\circ$ and $Z = 4$. Three-dimensional intensity data were collected on an automatic diffractometer. Atomic parameters were refined by full-matrix least-squares methods to a conventional R value of 0.04 for 2318 non-zero observed reflexions.

In this complex the diethyldithiocarbamate moiety acts as a monodentate ligand, the C—S double-bond distance being 1.68(1) Å and the C—S bond involving the sulphur atom that is coordinated to the gold atom being 1.75(1) Å. The gold atom is linearly coordinated, the S—Au—P angle being $175.7(1)^\circ$ and the Au—S and Au—P distances being 2.338(3) and 2.251(3) Å, respectively.

Introduction

The present compound, $(Ph_3P)Au(dtc)$, was prepared by Brinkhoff *et al.* (1971). The crystal structure analysis was undertaken to determine whether the gold atom is in three-fold coordination (with phosphine and bidentate dithiocarbamate) or in the usual two-fold coordination (with phosphine and monodentate dithiocarbamate moieties).

Experimental

Crystal data

Triphenylphosphine (*N,N*-diethyldithiocarbamato)gold(I), $(C_6H_5)_3PAuSSCN(C_2H_5)_2$ [$= (Ph_3P)Au(dtc)$], $FW = 607.5$. The well-formed yellow crystals are

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elongated along c with crystal forms $\{110\}$, $\{100\}$ and $\{001\}$. The crystals are monoclinic, space group $P2_1/c$ (No. 14) determined from systematic absences. From Pt-calibrated Weissenberg photographs around b and c using nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), application of a least-squares procedure yielded the unit cell dimensions: $a = 13.547(1)$, $b = 12.277(1)$, $c = 14.013(1) \text{ \AA}$, $\beta = 90.81(1)^\circ$; $V_c = 2330.4(5) \text{ \AA}^3$. The calculated density of 1.73 g cm^{-3} , with $Z = 4$, agrees with the measured value of 1.73 g cm^{-3} (flotation method). $F(000) = 1184$. The linear absorption coefficient for molybdenum $K\alpha$ radiation is $\mu = 67.7 \text{ cm}^{-1}$.

Intensity data

A crystal of approximate dimensions $0.05 \times 0.05 \times 0.6 \text{ mm}^3$ was mounted with c along the ϕ -axis of a Nonius automatic diffractometer. Intensity data were measured with Zr-filtered Mo-radiation using the moving-counter moving-crystal method with a scan speed of $1.2^\circ/\text{min}$. After every 20 reflexions a reference reflexion was measured to detect and allow corrections to be made for slow fluctuations in the primary beam. Of the 3738 attainable symmetry independent reflexions hkl (up to $\sin \theta/\lambda = 0.59 \text{ \AA}^{-1}$), 2193 reflexions have been measured above background. Of the 2015 attainable symmetry related reflexions hkl (up to $\sin \theta/\lambda = 0.48 \text{ \AA}^{-1}$), 1588 reflexions have been measured above background. (A reflexion is considered 'above background' if its peak intensity exceeds an instrumentally fixed value set slightly above the average background.) Absorption corrections were calculated according to the Busing & Levy (1957) procedure, using $6 \times 6 \times 4$ volume components and seven photographically located boundary planes (the absorption factors were in the range 1.36–1.41). The two symmetry-related sets of reflexions were brought on the same scale and corrected for L_p factors. The disagreement factor for reflexions common in both sets is:

$$R' = \frac{\sum |F_{hkl}| - |F_{h\bar{k}l}|}{\sum \frac{1}{2} [|F_{hkl}| + |F_{h\bar{k}l}|]} = 0.041$$

The variance of an observed structure amplitude was calculated as

$$\sigma_{hkl}^2 = \sigma_c^2 + (a' |F_{hkl}|)^2 \quad (1)$$

where σ_c is the standard deviation calculated from counting statistics, and a' is a constant, taken as 0.05. For weak reflexions the statistical errors in counting predominate, and therefore eqn. (1) gives better estimations of the variances of the weak reflexions than may be obtained by some well-known formulas (e.g. Hughes, 1941; Cruickshank, 1961). For strong reflexions the standard deviation given by eqn. (1) will become proportional to the observed structure amplitude. The value used for a' reflects our assumption of a 5% error in large structure amplitudes.

Eqn. (1) has been used also by Killeen (1969), but for simplicity we prefer not to interpret the physical meaning of a' and to guess its value. A generalization of eqn. (1), where a' is replaced by an intensity and scattering-angle dependent function determined from the deviations between symmetry-related intensities, has been published by Noordik (1971).

For the reflexions common in the symmetry-related sets of measurements, the weighted average $|\bar{F}|$ was calculated using weights obtained by eqn. (1). The variance $\sigma|\bar{F}|^2$ of the mean structure amplitude was calculated as either

$$\sigma^2|\bar{F}| = [\sigma_{hki}^{-2}(|\bar{F}| - |F_{hki}|)^2 + \sigma_{\bar{h}\bar{k}\bar{l}}^{-2}(|\bar{F}| - |F_{\bar{h}\bar{k}\bar{l}}|)^2] / [\sigma_{hki}^{-2} + \sigma_{\bar{h}\bar{k}\bar{l}}^{-2}]$$

or

$$\sigma^2|\bar{F}| = 1/[\sigma_{hki}^{-2} + \sigma_{\bar{h}\bar{k}\bar{l}}^{-2}] \quad (2)$$

whichever was the larger.

Structure determination

The structure was solved by Patterson and Fourier methods; the positions of all atoms (except hydrogen) were located. The positional and vibrational parameters and the scale factor were refined by full-matrix least-squares methods, allowing anisotropic vibration of the gold, sulphur and phosphorus atoms. The function that was minimized was $\sum w(|F_o| - |F_c|)^2$, with weight $w = \sigma^{-2}$ for each reflexion as obtained from eqn. (1) or (2). The atomic scattering factors were corrected for the anomalous scattering component $\Delta f'$ using data from the International Tables (1962). A conventional R value of 0.044 was obtained. The positions of the hydrogen atoms attached to the benzene rings and to C(2) and C(4) were calculated and included in the structure factor calculations with isotropic temperature factors equal to the temperature factors of the 'parent' carbon atoms. Two more least-squares refinement cycles reduced the conventional R value to 0.040 for 2318 non-zero observed reflexions. The parameter changes in the last cycle were only a small fraction of the standard deviations. A final difference Fourier synthesis showed some peaks of $0.5 \text{ e}\text{\AA}^{-3}$ on the expected positions of the hydrogen atoms attached to C(3) and C(5) but some other equally high peaks as well, so we did not include these hydrogen atoms in the structure factor calculations.

Calculations were performed on an IBM 360/50 computer using programs written by Busing *et al.* (1962), Johnson (1965), and Ahmed & Pippy (1968), and several programs written at this laboratory.

Results and discussion

The atomic parameters are given in tables 1 and 2. The structure is illustrated in figure 1, bond distances and angles are given in figure 2 and table 3.

The gold atom is in linear coordination, as usual for Au(I), the S(1)—Au—P angle being $175.7(1)^\circ$. The Au—S(1) and Au—P bond lengths are 2.338(3) and 2.251(3) Å, respectively. The deviation from strict linearity (4.3° , visible in figure 2) may be explained easily by the influence of the sulphur atom S(2); the Au...S(2) distance of 3.015(3) Å is somewhat less than the expected van der Waals distance (the sum of Pauling's van der Waals radius of S and the single-bond metallic radius of Au is 3.19 Å).

In contrast to its behaviour in many other structures, the dithiocarbamate

Table 1. Atomic parameters for (Ph₃P)Au(dtc) with standard deviations

(a) Au, S and P atoms with anisotropic temperature factors:

	$\exp(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)^*$								
	<i>x</i>	<i>y</i>	<i>z</i>	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Au	0.31576(3)	0.07432(4)	0.28038(3)	55.7(3)	64.3(4)	45.2(3)	-4.6(3)	-4.4(2)	-10.3(3)
S(1)	0.3029(2)	-0.0453(2)	0.1509(2)	56(2)	85(3)	58(2)	-8(2)	6(2)	-18(2)
S(2)	0.1351(2)	-0.0690(3)	0.2833(2)	72(2)	133(4)	53(2)	-38(2)	11(2)	-25(2)
P	0.3364(2)	0.1968(2)	0.3986(2)	53(2)	67(2)	47(2)	-7(2)	-1(1)	-8(2)

(b) N and C atoms with isotropic temperature factor parameters $B(\text{\AA}^2)$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
N	0.1376(6)	-0.1531(7)	0.1099(6)	4.4(2)	C(12)	0.233(1)	0.203(1)	0.481(1)	3.8(2)
C(1)	0.1852(7)	-0.0951(8)	0.1764(7)	3.6(2)	C(13)	0.215(1)	0.296(1)	0.533(1)	4.2(2)
C(2)	0.177(1)	-0.170(1)	0.012(1)	6.8(3)	C(14)	0.138(1)	0.298(1)	0.598(1)	4.8(2)
C(3)	0.132(1)	-0.089(1)	-0.053(1)	8.8(4)	C(15)	0.080(1)	0.205(1)	0.609(1)	4.4(2)
C(4)	0.039(1)	-0.201(1)	0.128(1)	5.5(3)	C(16)	0.098(1)	0.115(1)	0.559(1)	4.6(2)
C(5)	0.049(1)	-0.313(1)	0.167(1)	8.1(4)	C(17)	0.174(1)	0.110(1)	0.491(1)	4.4(2)
C(6)	0.347(1)	0.336(1)	0.356(1)	4.2(2)	C(18)	0.444(1)	0.174(1)	0.472(1)	3.7(2)
C(7)	0.281(1)	0.371(1)	0.286(1)	5.2(3)	C(19)	0.446(1)	0.194(1)	0.572(1)	5.4(3)
C(8)	0.284(1)	0.477(1)	0.253(1)	6.2(3)	C(20)	0.534(1)	0.178(1)	0.626(1)	5.7(3)
C(9)	0.353(1)	0.549(1)	0.292(1)	6.1(3)	C(21)	0.615(1)	0.146(1)	0.582(1)	5.6(3)
C(10)	0.420(1)	0.518(1)	0.357(1)	6.6(3)	C(22)	0.617(1)	0.125(1)	0.487(1)	7.3(3)
C(11)	0.418(1)	0.409(1)	0.391(1)	5.6(3)	C(23)	0.528(1)	0.137(1)	0.430(1)	5.7(3)

* The anisotropic vibration parameters correspond to an average r.m.s. displacement of 0.22 Å, except for the atom S(2), having a r.m.s. displacement of 0.36 Å about normal to the plane of the (dtc) ligand.

The key to atomic numbering is given in figure 2. The hydrogen positions are given in table 2.

Table 2. *Calculated positions of the hydrogen atoms*

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
H(2a)	0.163	-0.252	-0.014	H(10)	0.472	0.578	0.390
H(2b)	0.260	-0.158	0.009	H(11)	0.478	0.382	0.438
H(3a)*	0.052	-0.090	-0.041	H(13)	0.267	0.370	0.518
H(3b)*	0.147	-0.110	-0.126	H(14)	0.128	0.371	0.644
H(3c)*	0.160	-0.008	-0.037	H(15)	0.017	0.215	0.656
H(4a)	-0.003	-0.204	0.064	H(16)	0.058	0.037	0.573
H(4b)	0.001	-0.149	0.181	H(17)	0.197	0.038	0.449
H(5a)*	-0.023	-0.345	0.185	H(19)	0.388	0.242	0.601
H(5b)*	0.095	-0.311	0.232	H(20)	0.526	0.186	0.707
H(5c)*	0.083	-0.365	0.114	H(21)	0.689	0.153	0.619
H(7)	0.226	0.311	0.266	H(22)	0.684	0.081	0.460
H(8)	0.230	0.505	0.194	H(23)	0.534	0.131	0.354
H(9)	0.351	0.633	0.265				

Atoms not included in the structure factor calculations are indicated by asterisks. The numbers of the atoms refer to the parent carbon atoms.

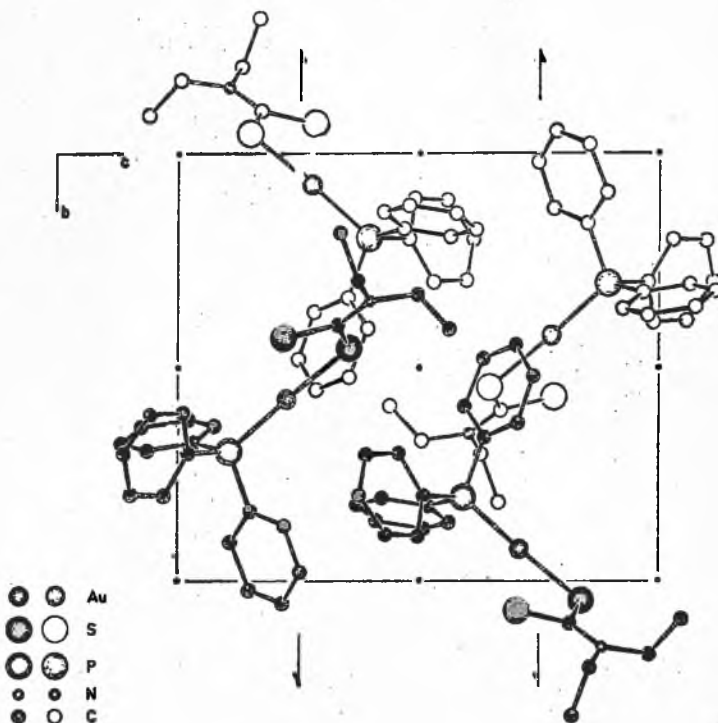


Fig. 1. Projection of the structure of $Ph_3PAu(dtc)$ along *a*. Centres of symmetry and two-fold screw axes are indicated.

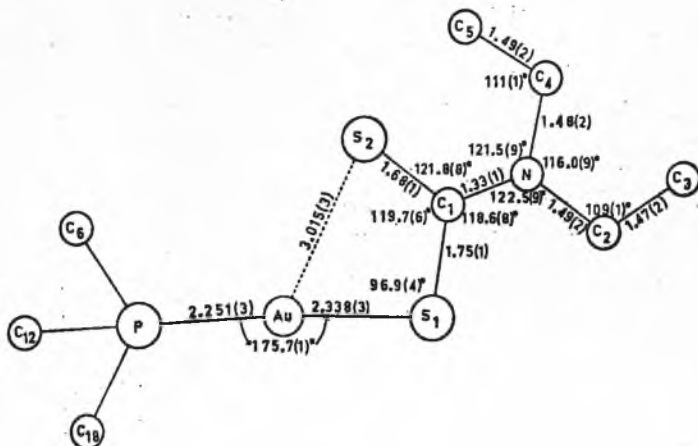


Fig. 2. Dimensions of the (dtc)-ligand and the coordination of the gold atom. Dimensions of the Ph₃P-ligand are given in table 3.

group acts as a monodentate ligand, S(1) being bonded to the gold atom, while the S(2)···Au distance is as much as 3.015 Å. Relative to the normal situation, where the two C—S bonds have partial double bond character, the present situation may be represented by a weakening of the C(1)—S(1) bond and the formation of a C(1)—S(2) double bond. This is shown by the highly significant difference in the bond lengths C(1)—S(1), 1.75(1) Å and C(1)—S(2), 1.68(1) Å, whereas the average C—S bond for dithiocarbamate-gold complexes is 1.71 Å (Noordik & Beurskens, 1971). In table 4, some distances found in asymmetrically bonded dithiocarbamates are given.

The equation of the least-squares plane through S(1), S(2), C(1) and N is given by

$$-0.4027X + 0.8384Y - 0.3672Z + 2.8827 = 0$$

referred to an orthogonal axes system with *X* along *a* and *Z* along *c**; the deviations from this plane are for C(2), 0.11(1) and for C(4), -0.05(1) Å. The Au atom is about 0.5 Å out of this plane, which again is in contrast to most dithiocarbamate complexes.

The Au—S(1) distance, 2.338(3) Å, agrees very well with the average Au—S distance of 2.333 Å found in other dithiocarbamate-gold complexes (Noordik & Beurskens, 1971).

The triphenylphosphine ligand is in the usual trigonal-pyramidal configuration. The best planes through the three benzene rings are given as follows:

$$\text{plane 1: C(6)—C(11): } 0.6447X - 0.2709Y - 0.7148Z + 1.6870 = 0$$

$$\text{plane 2: C(12)—C(17): } -0.6151X + 0.3261Y - 0.7179Z + 5.9037 = 0$$

$$\text{plane 3: C(18)—C(28): } 0.2597X + 0.9495Y - 0.1759Z - 2.3939 = 0$$

Table 3. Bond distances and angles in the (Ph₃P) ligand with standard deviations

Distances and angles involving phosphorus								
P—C(6)	1.81(1) Å	P—C(12)	1.83(1) Å	P—C(18)	1.79(1) Å			
Au—P—C(6)	113.2(4)°	Au—P—C(12)	113.9(4)°	Au—P—C(18)	114.1(4)°			
C(6)—P—C(12)	103.3(5)°	C(12)—P—C(18)	105.6(5)°	C(18)—P—C(6)	105.8(5)°			
P—C(6)—C(7)	118.4(8)°	P—C(12)—C(13)	121.0(8)°	P—C(18)—C(19)	122.8(8)°			
P—C(6)—C(11)	122.7(8)°	P—C(12)—C(17)	118.3(8)°	P—C(18)—C(23)	118.5(8)°			
Distances in benzene rings, all ±0.02 Å								
C(6)—C(7), ...,	C(11)—C(6):	1.38,	1.39,	1.38,	1.33,	1.42	and	1.40 Å
C(12)—C(13), ...,	C(17)—C(12):	1.37,	1.39,	1.40,	1.34,	1.41	and	1.40 Å
C(18)—C(19), ...,	C(23)—C(18):	1.43,	1.41,	1.34,	1.35,	1.45	and	1.37 Å
Angles in benzene rings, all ±1°								
C(11)—C(6)—C(7), C(6)—C(7)—C(8), ...:	119,	120,	119,	122,	119	and	120°	
C(17)—C(12)—C(13), ...:	121,	120,	119,	120,	122	and	118°	
C(23)—C(18)—C(19), ...:	119,	120,	119,	122,	120	and	119°	

Table 4. *Some distances in asymmetrically bonded dithiocarbamate complexes. (Å)*

M	M—S(1)	M—S(2)	S(1)—C	S(2)—C	Compound	Note
Au	2.324(5)	2.329(5)	1.73(2)	1.69(2)	Au(dtc)(S ₂ C ₄ N ₂)	1
Sn	2.48(1)	2.79(1)	1.68(4)	1.74(4)	(CH ₃) ₂ ClSn(dtc)	2
Te	2.498(7)	2.856(8)	1.76(3)	1.69(2)	Te(dtc) ₂	3
Se	2.332(4)	2.779(5)	1.75(2)	1.65(2)	Se(dtc) ₂	4
As	2.322(6)	2.835(6)	1.76(2)	1.69(2)	C ₆ H ₅ As(dtc) ₂	5
	2.330(6)	2.911(6)	1.78(2)	1.65(2)		
As	2.351(3)	2.903(4)	1.76(1)	1.68(1)	As(dtc) ₃	6
	2.336(2)	2.820(3)				
	2.358(3)	2.810(3)				
Sn	2.47(1)	3.16(1)	1.80(2)	1.70(3)	(CH ₃) ₂ Sn(dtc)	7
	2.47(1)	3.33(1)	1.78(3)	1.71(3)		
Au	2.338(3)	3.015(3)	1.75(1)	1.68(1)	Ph ₃ PAu(dtc)	8
Ru	2.398	3.633			Ru(NO)(dtc)	9
—				1.63	R ₄ N ₂ C ₂ S ₄	10

Notes: (dtc) = S₂CNR₂ with R = CH₃, C₂H₅, C₄H₉ or $\frac{1}{2}$ (OC₄H₉).

(1) The slight asymmetry of the (dtc) ligand is caused by interactions from a neighbouring molecule (Noordik, 1971).

(2) The difference in S—C distances, albeit non-significant, is in contrast to other entries in this table (Furue *et al.*, 1970).

(3) Husebye, 1970.

(4) Husebye & Helland-Madsen, 1970.

(5) Bally, 1967.

(6) The given S—C distances are averaged (Colapietro *et al.*, 1968).

(7) The given distances apply to two crystallographically independent molecules (Sheldrick & Sheldrick, 1970).

(8) This work.

(9) The given distances apply to the one monodentate (dtc) ligand; S—C distances were not reported (Domenicano *et al.*, 1966).

(10) Average S—C distance in (CH₃)₄N₂S₂C₄ (1.61 Å) (Marøy, 1965), and in (C₂H₅)₄N₂S₂C₄ (1.63 and 1.66 Å) (Karle *et al.*, 1967).

The angles between the planes 1 and 2, 2 and 3 and 3 and 1 are 88°23', 73°58' and 87°57', respectively. Bond angles and distances within the ligand agree with those found in other triphenylphosphine derivatives.

Despite the irregular shape of the molecule, there exists a reasonably close packing in the crystal. The packing coefficient was calculated to be 0.689. For triphenylmethane, it is 0.638; other polyphenyls range from 0.685 to 0.746 (Kitaigorodskii, 1961). There are no unusual intermolecular interactions. The shortest intermolecular distance is Au...C(21) = 3.44 ± 0.01 Å.

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