using *SHELXTL* (Sheldrick, 1978) on a data General Eclipse 140 computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles, along with a crystal packing diagram, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71605 (43 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1067]

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(*o*-Methoxybenzenethiolato)(triphenylphosphine)gold(I) Diethyl Ether Solvate

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(*Received* 19 *March* 1993; *accepted* 15 *November* 1993)

Abstract

The crystal structure of $[Au(C_7H_7OS)(C_{18}H_{15}P)].0.25C_4H_{10}O$ contains two Au^I centers; each Au^I is almost linearly coordinated [P—Au—S bond angles of 175.2 (1) and 176.2 (1)°] and a large $Au^I \cdots Au^I$ intramolecular distance of 5.741 (3) Å is found.

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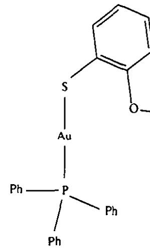
Comment

Gold(I) compounds with sulfur-containing ligands are used in the treatment of rheumatoid arthritis (Brown & Smith, 1980). This chemistry has been expanded to include phosphine–sulfur gold complexes through the development of Auranofin as a successful drug (Parish & Cottrill, 1987). As part of our continuing effort to understand the basic chemistry of gold(I)–sulfur compounds, we have determined the structure of $[Au(PPh_3)(SPh\text{-}o\text{-}OMe)]$ (I). Compound (I) was prepared by the method reported by Baenziger, Dittemore & Doyle (1974). The compound is shown in Fig. 1.



(I)

Compound (I) crystallizes with an Au···Au separation of 5.741 (3) Å and P—Au—S angles showing linear geometry [175.2 (1) and 176.2 (1)°]. We have determined (Fackler, Staples, Elduque & Grant, 1994) the structure of $[Au(SPh)(PPh_3)]$ which crystallized in dinuclear fragments with an Au···Au interaction of 3.154 (2) Å and P—Au—S angles of 179.0 (1) and 175.9 (1)°. Some related structures have been compared by Muir, Cuadrado & Muir (1988), in their report of the structure of (2-benzoxazolethiolato)(triphenylphosphine)gold(I), $[Au(Sboz)(PPh_3)]$.

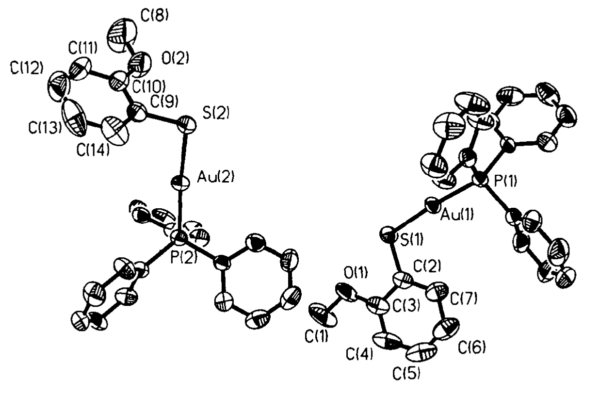


Fig. 1. A drawing of the two molecules of $[Au(PPh_3)SPh\text{-}o\text{-}OMe]$, showing the atomic labeling scheme with displacement ellipsoids drawn at 50% probability. The Au(1)···Au(2) distance is 5.741 (2) Å.

Crane & Beall (1978) stated that a P—Au—S angle of 173.5° is evidence of Au···Au attraction. The angles and the Au···Au interaction reported here for (I) agree with this observation in that a longer Au···Au interaction corresponds to a more linear arrangement. One might infer from this observation that the lack of Au···Au interaction in (I) is caused by the steric bulk of the methoxybenzenethiolato ligand. However, this does not agree with the results reported by Cookson & Tiekink (1993) who compared the structure of $[Au(2\text{-}Spy)(PPh_3)]$ (2-Spy = pyridine-2-thiol) with those of related triorganophosphinegold(I) thiolates. They observed that the angles ranged from 172 to 178° and that there was no Au···Au interaction as observed for $[Au(SPh)(PPh_3)]$. The structures reported by Cookson & Tiekink are similar to the structure reported here.

This lack of a gold–gold interaction for the methoxybenzenethiolate and the pyridine-2-thiolate complexes of $[AuPPh_3]^+$ is most likely the result of an electronic effect on the thiol ligands rather than a result of their steric bulk. This electronic effect, which seems to be of significance in these cases, appears to depend on the σ-donation ability of the thiolate ligand. We have looked at the electronic factors involved in the formation of three-coordinate gold(I) bisphosphine xanthate complexes (Assefa, Staples & Fackler, 1993). The solvent molecule does not appear to interfere with the possible gold–gold interaction.

Experimental

Crystal data

$[Au(C_7H_7OS)(C_{18}H_{15}P)]$.-
$0.25C_4H_{10}O$
$M_r = 616.98$
Triclinic
$P\bar{1}$
$a = 12.319$ (1) Å
$b = 18.236$ (2) Å
$c = 10.883$ (1) Å
$\alpha = 94.468$ (7)°
$\beta = 97.417$ (7)°
$\gamma = 98.720$ (7)°
$V = 2384.5$ (4) Å^3
$Z = 4$
$D_x = 1.71$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 32\text{-}35°$
$\mu = 6.32$ mm^{-1}
$T = 293$ K
Rectangular
0.1 × 0.2 × 0.4 mm
Colorless
Crystal source: CH_2Cl_2/Et_2O

Data collection

R3m/E diffractometer
Wycoff scans
Absorption correction: empirical
$T_{min} = 0.41$, $T_{max} = 0.98$
6415 measured reflections
6199 independent reflections
4596 observed reflections $[F_o^2 > 3\sigma(F_o^2)]$
$\theta_{max} = 25°$
$h = 0 \rightarrow 14$
$k = -20 \rightarrow 20$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 97 reflections
intensity variation: <1%

Refinement

Refinement on F
$R = 0.0266$
$wR = 0.0271$
$S = 1.00$
4596 reflections
535 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.0041F_o^2]$
$(\Delta/\sigma)_{max} = 0.025$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Au(1)	0.2345 (1)	0.0483 (1)	0.0127 (1)	0.037 (1)
Au(2)	0.0621 (1)	0.3735 (1)	0.6271 (1)	0.040 (1)
S(1)	0.3515 (2)	0.0806 (1)	0.2006 (2)	0.049 (1)
S(2)	−0.1222 (2)	0.3469 (1)	0.5443 (2)	0.056 (1)
P(1)	0.1315 (1)	0.0213 (1)	−0.1799 (2)	0.035 (1)
P(2)	0.2461 (2)	0.3937 (1)	0.6996 (2)	0.038 (1)
O(1)	0.5407 (4)	0.1595 (3)	0.3712 (5)	0.067 (2)
O(2)	−0.2701 (5)	0.3134 (3)	0.7272 (6)	0.082 (3)
C(1)	0.6239 (8)	0.1918 (6)	0.4725 (9)	0.114 (5)
C(2)	0.4838 (6)	0.1119 (4)	0.1588 (7)	0.044 (3)
C(3)	0.5684 (6)	0.1504 (4)	0.2544 (8)	0.053 (3)
C(4)	0.6728 (6)	0.1753 (4)	0.2272 (9)	0.069 (4)
C(5)	0.6956 (7)	0.1620 (5)	0.1058 (9)	0.079 (4)
C(6)	0.6175 (7)	0.1242 (5)	0.0134 (9)	0.074 (4)
C(7)	0.5097 (7)	0.0987 (4)	0.0398 (8)	0.060 (3)
C(8)	−0.3424 (11)	0.2862 (7)	0.8097 (12)	0.162 (8)
C(9)	−0.1837 (6)	0.4120 (4)	0.6345 (6)	0.047 (3)
C(10)	−0.2573 (6)	0.3867 (4)	0.7147 (7)	0.058 (3)
C(11)	−0.3109 (7)	0.4382 (5)	0.7769 (10)	0.088 (4)
C(12)	−0.2956 (8)	0.5105 (5)	0.7601 (10)	0.095 (5)
C(13)	−0.2243 (9)	0.5377 (5)	0.6874 (9)	0.097 (5)
C(14)	−0.1690 (8)	0.4882 (5)	0.6217 (8)	0.077 (4)
C(15)	0.0670 (5)	−0.0751 (3)	−0.2234 (6)	0.033 (2)
C(16)	0.0241 (6)	−0.1146 (4)	−0.1356 (7)	0.056 (3)
C(17)	−0.0250 (7)	−0.1901 (5)	−0.1674 (10)	0.077 (4)
C(18)	−0.0272 (8)	−0.2257 (5)	−0.2840 (9)	0.077 (4)
C(19)	0.0136 (7)	−0.1869 (4)	−0.3723 (8)	0.068 (4)
C(20)	0.0617 (6)	−0.1116 (4)	−0.3431 (7)	0.052 (3)
C(21)	0.2244 (5)	0.0409 (4)	−0.2934 (6)	0.039 (3)
C(22)	0.1956 (7)	0.0768 (4)	−0.3958 (6)	0.053 (3)
C(23)	0.2705 (8)	0.0900 (5)	−0.4781 (7)	0.072 (4)
C(24)	0.3741 (7)	0.0670 (5)	−0.4591 (8)	0.071 (4)
C(25)	0.4002 (7)	0.0306 (5)	−0.3599 (7)	0.064 (4)
C(26)	0.3262 (6)	0.0178 (4)	−0.2752 (7)	0.052 (3)
C(27)	0.0233 (5)	0.0764 (4)	−0.2127 (6)	0.040 (3)
C(28)	0.0500 (6)	0.1532 (4)	−0.1858 (7)	0.055 (3)
C(29)	−0.0244 (7)	0.1993 (5)	−0.2170 (8)	0.067 (4)
C(30)	−0.1314 (7)	0.1668 (5)	−0.2751 (9)	0.083 (4)
C(31)	−0.1607 (7)	0.0906 (5)	−0.2977 (10)	0.087 (5)
C(32)	−0.0834 (6)	0.0456 (4)	−0.2667 (7)	0.060 (3)
C(33)	0.3013 (5)	0.4908 (4)	0.7633 (6)	0.040 (3)
C(34)	0.2471 (6)	0.5461 (4)	0.7201 (7)	0.054 (3)
C(35)	0.2881 (7)	0.6203 (4)	0.7655 (8)	0.062 (3)
C(36)	0.3825 (6)	0.6407 (4)	0.8523 (7)	0.050 (3)
C(37)	0.4367 (6)	0.5857 (4)	0.8951 (7)	0.053 (3)
C(38)	0.3979 (6)	0.5113 (4)	0.8510 (7)	0.050 (3)
C(39)	0.2832 (5)	0.3393 (4)	0.8251 (6)	0.039 (2)
C(40)	0.2400 (6)	0.3523 (4)	0.9375 (7)	0.046 (3)
C(41)	0.2644 (7)	0.3096 (4)	1.0305 (7)	0.060 (3)
C(42)	0.3270 (7)	0.2541 (4)	1.0173 (8)	0.067 (3)
C(43)	0.3663 (7)	0.2406 (4)	0.9062 (7)	0.062 (3)
C(44)	0.3452 (6)	0.2827 (4)	0.8102 (7)	0.053 (3)
C(45)	0.3271 (5)	0.3679 (4)	0.5791 (6)	0.039 (2)
C(46)	0.4281 (6)	0.4092 (4)	0.5653 (7)	0.055 (3)
C(47)	0.4868 (7)	0.3858 (5)	0.4737 (8)	0.067 (4)
C(48)	0.4441 (7)	0.3202 (5)	0.3927 (8)	0.067 (4)
C(49)	0.3453 (7)	0.2793 (5)	0.4036 (7)	0.066 (4)

C(50)	0.2855 (6)	0.3032 (4)	0.4963 (7)	0.052 (3)
O(1*s*)	−0.0286 (22)	0.5234 (19)	1.0370 (23)	0.184 (10)
C(1*s*)	−0.0389 (21)	0.4548 (16)	1.0297 (23)	0.241 (11)
C(2*s*)	−0.0500 (16)	0.3829 (11)	1.0445 (18)	0.228 (9)

Table 2. *Selected geometric parameters* (Å, °)

Au(1)—S(1)	2.324 (2)	Au(2)—P(2)	2.266 (2)
Au(2)—S(2)	2.296 (2)	S(2)—C(9)	1.797 (8)
S(1)—C(2)	1.773 (7)	P(1)—C(21)	1.808 (7)
P(1)—C(15)	1.816 (6)	P(2)—C(33)	1.845 (6)
P(1)—C(27)	1.803 (7)	P(2)—C(45)	1.822 (7)
P(2)—C(39)	1.802 (7)	O(1)—C(3)	1.363 (10)
O(1)—C(1)	1.427 (10)	O(2)—C(10)	1.341 (10)
O(2)—C(8)	1.410 (15)	C(2)—C(7)	1.385 (11)
C(2)—C(3)	1.430 (9)	C(4)—C(5)	1.397 (14)
C(3)—C(4)	1.375 (11)	C(6)—C(7)	1.413 (12)
C(5)—C(6)	1.361 (11)	C(9)—C(14)	1.394 (12)
C(9)—C(10)	1.392 (11)	C(11)—C(12)	1.333 (14)
C(10)—C(11)	1.408 (13)	C(13)—C(14)	1.415 (15)
C(12)—C(13)	1.324 (15)	O(1s)—C(1s)	1.233 (44)
Au(1)—P(1)	2.283 (2)	C(1s)—C(2s)	1.323 (35)
S(1)—Au(1)—P(1)	175.2 (1)	C(39)—P(2)—C(45)	104.7 (3)
Au(1)—S(1)—C(2)	105.0 (2)	C(8)—O(2)—C(10)	117.3 (8)
Au(1)—P(1)—C(15)	116.8 (2)	S(1)—C(2)—C(7)	123.2 (5)
C(15)—P(1)—C(21)	104.4 (3)	O(1)—C(3)—C(2)	117.0 (6)
C(15)—P(1)—C(27)	106.0 (3)	C(2)—C(3)—C(4)	120.2 (8)
Au(2)—P(2)—C(33)	113.9 (2)	C(4)—C(5)—C(6)	121.8 (8)
C(33)—P(2)—C(39)	104.2 (3)	C(2)—C(7)—C(6)	120.2 (7)
C(33)—P(2)—C(45)	108.2 (3)	S(2)—C(9)—C(14)	123.3 (6)
C(1)—O(1)—C(3)	119.7 (6)	O(2)—C(10)—C(9)	115.8 (7)
S(1)—C(2)—C(3)	117.8 (6)	C(9)—C(10)—C(11)	119.1 (8)
C(3)—C(2)—C(7)	119.0 (7)	C(11)—C(12)—C(13)	120.8 (10)
O(1)—C(3)—C(4)	122.8 (7)	C(9)—C(14)—C(13)	122.3 (9)
C(3)—C(4)—C(5)	119.4 (7)	P(1)—C(15)—C(20)	123.3 (5)
C(5)—C(6)—C(7)	119.5 (9)	P(1)—C(21)—C(22)	121.9 (6)
S(2)—C(9)—C(10)	120.2 (6)	P(1)—C(27)—C(28)	118.1 (5)
C(10)—C(9)—C(14)	116.3 (8)	P(2)—C(33)—C(34)	118.1 (5)
O(2)—C(10)—C(11)	125.1 (8)	P(2)—C(39)—C(40)	117.8 (5)
C(10)—C(11)—C(12)	122.4 (9)	P(2)—C(45)—C(46)	122.6 (5)
C(12)—C(13)—C(14)	118.9 (9)	C(1*s*)—O(1*s*)—O(1*sa*)	53.2 (26)
P(1)—C(15)—C(16)	118.6 (5)	O(1*s*)—C(1*s*)—C(2*s*)	169.4 (27)
S(2)—Au(2)—P(2)	176.2 (1)	P(1)—C(21)—C(26)	118.1 (5)
Au(2)—S(2)—C(9)	103.0 (2)	P(1)—C(27)—C(32)	122.9 (5)
Au(1)—P(1)—C(21)	107.4 (2)	P(2)—C(33)—C(38)	123.5 (6)
Au(1)—P(1)—C(27)	115.5 (2)	P(2)—C(39)—C(44)	121.7 (6)
C(21)—P(1)—C(27)	105.7 (3)	P(2)—C(45)—C(50)	118.9 (5)
Au(2)—P(2)—C(39)	113.7 (2)	C(1*s*)—O(1*s*)—C(1*sa*)	107.5 (28)
Au(2)—P(2)—C(45)	111.4 (2)		

The ether molecule is generated by an inversion center located at $0,\frac{1}{2},0$ such that the O atom was placed at 50% occupancy. Atoms in the ether molecule are the only non-H atoms to be modeled isotropically. Calculations were performed using *SHELXTL* (Sheldrick, 1978) on a Data General Eclipse 140 computer.

We acknowledge support from the Robert A. Welch Foundation, A-0960, and the National Science Foundation, CHE-8708625, for this study.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71576 (48 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1072]

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Acta Cryst. (1994). C**50**, 525–528

Dichloro(2,6-diacetylpyridine dioxime-κ^3N,N',N'')copper(II) 1.5-Hydrate

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(*Received* 4 *March* 1993; *accepted* 15 *September* 1993)

Abstract

The reaction of hydroxylamine with aquachloro-(2,6-diacetylpyridine disemicarbazone)copper(II) results in a displacement of the semicarbazide group and the formation of dichloro(2,6-diacetylpyridine dioxime-κ^3N,N',N'')copper(II) 1.5-hydrate {$[CuCl_2(C_9H_{11}N_3O_2)]_2.3H_2O$}. A triclinic dihydrate form has been reported previously. The Cu atom is in the center of a square pyramid consisting of a Cl and three N atoms in the base and an apical Cl. An analysis of the five-coordinate $CuCl_2N_3$ structures in the 1992 release of the Cambridge Crystallographic Database revealed a linear relationship between the displacement of the Cu atom from the basal plane and the apical Cu—Cl distance.

Comment

Dichloro(2,6-diacetylpyridine dioxime-κ^3N,N',N'')-copper(II) dihydrate (I), $[CuCl_2(dapdH_2)].2H_2O$, was reported by Nicholson, Petersen & McCormick (1982) to crystallize in a triclinic form with one molecule per asymmetric unit. Our form is found to be monoclinic with two molecules of $CuCl_2(DAPDH_2).1.5H_2O$ per asymmetric unit (see Fig. 1). The analytical data for C, H and N are in agreement with 1.5 waters per Cu atom: found (calculated) C