significant bonding interactions. The Hg-atom geometry is thus best described as being approximately *T*-shaped with S—Hg—S angles of 165, 100 and 95°.

The remaining xanthate ligand geometries are as expected. The C—S bond distances are not equivalent with the longer bonds being associated with the S atoms more strongly coordinated to the Hg atom.

The polymeric structure reported here for $Hg(S_2COCH_3)_2$ resembles those noted earlier for the related 1,1-dithiolate derivatives $Hg[S_2P(O^iC_3H_7)_2]_2$ (Lawton, 1971) and $Te(S_2COC_2H_5)Br$ (Gable, Hoskins, Steen & Winter, 1983). In the Hg compound bridging dithiophosphate ligands lead to a zigzag chain, as in $Hg(S_2COCH_3)_2$; however, the remaining dithiophosphate ligand chelates the Hg atom so that approximate tetrahedral coordination about the central atom is retained. In contrast, the backbone of the helical structure in $Te(S_2COC_2H_5)Br$ comprises Te and bridging Br atoms; the xanthates function as chelating ligands so that each Te atom in the polymer is four-coordinate.

Whereas in the previously reported Hg 1,1-dithiolates described above and in the closely related $Hg[S_2CN(C_2H_5)_2]_2$ compounds (Iwasaki, 1973) the Hg atoms exist in distorted tetrahedral environments, the Hg atom in $Hg(S_2COCH_3)_2$ has been shown to be three-coordinate. A similar decrease in coordination number has also been recently noted for the tris(xanthates) of Bi^{III}. In $Bi(S_2CO^iC_3H_7)_3$ (Hoskins, Tiekink & Winter, 1985) bridging xanthate ligands lead to a polymeric structure with seven-coordinate Bi; however, for the methyl analogue (Snow & Tiekink, 1986) two centrosymmetrically related molecules only loosely associate *via* weak Bi···S interactions of 3·405 (1) Å so that the Bi atoms must be considered six-coordinate. It would seem that the presence of the $^-S_2COCH_3$ anion in the $Hg(S_2COCH_3)_2$ and $Bi(S_2COCH_3)_3$ compounds decreases the Lewis acidity of the central atoms. These observations may indicate a different coordinating ability of the methylxanthate anion compared with higher homologues.

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Chloro(triphenylphosphine sulfide)gold(I)

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Abstract. $[\{(C_6H_5)_3PS\}AuCl]$, $M_r = 526·8$, monoclinic, $P2_1/n$, $a = 12·286$ (2), $b = 9·447$ (1), $c = 14·814$ (2) Å, $\beta = 94·39$ (2)°, $V = 1714·4$ (3) Å^3, $Z = 4$, $D_m = 2·025$ (7), $D_x = 2·041$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 89·26$ cm^{-1}, $F(000) = 1000$, room temperature, $R = 0·024$, 3008 unique reflections. The structure consists of monomeric $[(Ph_3PS)AuCl]$ molecules with linear gold(I) having an S—Au—Cl angle

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of 175·59 (5)°, and Au—S and Au—Cl distances of 2·256 (1) and 2·555 (1) Å. The Au—Cl length is markedly longer than that observed in other linear gold(I) complexes with chloride coordinated *trans* to S donors.

Introduction. Several gold(I) complexes have been used as effective drugs in chemotherapy and a range of these complexes with SH or S^- groups is known which are in commercial use (Empire Rheumatism Council, 1961). The *in vivo* distribution and therapeutic activity of these drugs is altered by changing the structures of the complex and its conditions of administration (Freyberg, Ziff & Baum, 1972; Brown, McKinley & Smith, 1978). This led to an extensive search for stable, preferably water-soluble, gold complexes of improved activity and reduced toxicity (Sadler, 1976; Waltz, DiMartino & Sutton, 1974) and several successful studies of the use of Et_3PAuCl in gold therapy are reported (Finkelstein, Waltz, Batista, Mixraji, Roisman & Misher, 1976; Waltz *et al.*, 1974). Unlike standard mercapto-gold drugs, which are administered by intramuscular injections, the Et_3PAuCl complex is orally effective and thus has advantages due to its ease of administration. In addition to Et_3PAuCl, several other phosphine complexes of the type R_3PAuL have been prepared starting with R_3PAuCl, and were found to be orally active in clinical trials (Waltz *et al.*, 1974; Brown & Smith, 1980).

The crystal structure of none of these drugs is known. On the basis of spectroscopic data, gold(I) is assumed to have a linear geometry. Since complexes with different types of ligands have been successfully used, it has been suggested that it is the metal ion which is the active moiety in these drugs (Preston, Block & Freyberg, 1942).

As a part of our continuing research program (Hussain & Isab, 1984, 1985*a*,*b*; Isab & Hussain, 1985, 1986) dealing with structure and chemistry of chemical models for anti-arthritic agents, we report here the synthesis, crystal and molecular structure of chloro(triphenylphosphine sulfide)gold(I) which has an S donor in addition to being structurally related to the orally effective gold drug Et_3PAuCl. It is perhaps surprising that the crystal structures of only a few S–Au complexes are known (Jones, 1981, 1983, 1986). The present crystal structure analysis is likely to aid in understanding the chemistry of related gold drugs.

Experimental. The compound was prepared by stirring a slight excess over the equimolar ratio of solid triphenylphosphine sulfide with an ethanolic solution of $HAuCl_4$ for several hours under a nitrogen atmosphere. The yellow solution became colorless as Au^{III} was reduced to Au^{I}. On leaving this solution in the refrigerator for several days, transparent crystals of the title complex separated from the solution. The infrared spectra recorded on a Perkin–Elmer 180 spectrophotometer using KBr pellets clearly revealed IR absorptions associated with the free triphenylphosphine sulfide. A naturally grown approximately spherical crystal was used for diffraction data. The cell parameters are given in the *Abstract* while the intensity data collection, structure solution and refinement parameters are listed in Table 1. The final atomic coordinates and B_{eq} values are given in Table 2.*

Discussion. A perspective molecular view with the atomic numbering scheme is shown in Fig. 1. The hydrogen-atom numbering follows that of the carbon atoms to which they are attached. The interatomic distances and angles are listed in Table 3. The structure consists of monomeric $[(Ph_3PS)AuCl]$ units separated by normal van der Waals contacts with the shortest intermolecular contact being Au···C(14) at 3·576 (6) Å.

A comparison of the Au—Cl bond length [2·555 (1) Å] with similar bonds shows a marked elongation of about 0·28 Å from the 2·273–2·279 Å observed in other linear gold(I) complexes with chloride coordinated *trans* to P, Se and even S donors (Table 4).

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles in the phenyl rings and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43469 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Data collection and structure refinement parameters for the title complex*

Crystal shape	Spherical
Method of measuring crystal density	Flotation
Diffractometer used	CAD-4
Method of intensity measurement	ω–2θ
No. and 2θ range of reflections for lattice parameters	25 $> 23°$
Absorption coefficient (μ) cm^{-1}	89·3
Rel. maximum transmission factor	100
Rel. minimum transmission factor	53
Rel. average transmission factor	81
Range of h, k and l	$0\rightarrow14$, $0\rightarrow11$, $-17\rightarrow17$
Interval, std. reflections measured	100
Total No. of reflections measured; 2θ range	3786; $2·0 < 2\theta < 60·0°$
No. of unique reflections; R_{int}	3008; 0·001
No. of observed reflections	2492
Criterion for observed reflections	$I > 2\sigma(I)$
Methods used to solve structure	Patterson/Difference Fourier
Use of F or F^2 in LS refinement	F
Method of locating hydrogens	ΔF map
Weighting scheme	$1/\sigma^2$*
Parameters refined	200
Value of R	0·024
Value of wR	0·033
Ratio of max. LS shift to e.s.d. (Δ/σ)	0·04
Max. height in final ΔF map	$<0·49$ (15) e $Å^{-3}$
Error in an observation of unit weight	1·202
Extinction coefficient	$2·110 \times 10^{7}$
Sources of atomic scattering factors and f', f'' values	*International Tables for X-ray Crystallography* (1974)
Computer programs used	*SDP* (Frenz, 1980)

* $\sigma^2 = \sigma^2_{(counting)} + (pF_o^2)^2$ where $p = 0·04$.

Table 2. *Positional parameters*

Hydrogen atoms were not refined. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\alpha)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B_{eq}(Å^2)
Au	0·17781 (1)	0·06496 (2)	0·06999 (1)	3·280 (4)
Cl	0·2404 (1)	0·0598 (2)	0·21708 (9)	5·09 (3)
S	0·1080 (1)	0·0547 (1)	−0·07521 (9)	3·74 (3)
P	0·17240 (8)	0·2197 (1)	−0·13930 (7)	2·36 (2)
C(1)	0·3177 (3)	0·2081 (4)	−0·1451 (3)	2·34 (8)
C(2)	0·3751 (4)	0·0862 (5)	−0·1170 (3)	3·02 (9)
C(3)	0·4867 (4)	0·0803 (5)	−0·1248 (4)	3·9 (1)
C(4)	0·5403 (4)	0·1928 (6)	−0·1615 (4)	4·1 (1)
C(5)	0·4830 (4)	0·3123 (6)	−0·1888 (4)	4·0 (1)
C(6)	0·3731 (4)	0·3226 (5)	−0·1806 (3)	3·34 (9)
C(7)	0·1065 (3)	0·2115 (5)	−0·2521 (3)	2·59 (8)
C(8)	−0·0065 (4)	0·1951 (5)	−0·2609 (3)	3·3 (1)
C(9)	−0·0605 (4)	0·1830 (6)	−0·3443 (3)	3·8 (1)
C(10)	−0·0021 (4)	0·1851 (6)	−0·4214 (3)	3·9 (1)
C(11)	0·1076 (4)	0·2029 (6)	−0·4134 (3)	3·8 (1)
C(12)	0·1634 (4)	0·2154 (5)	−0·3285 (3)	3·17 (9)
C(13)	0·1461 (3)	0·3899 (5)	−0·0914 (3)	2·42 (8)
C(14)	0·1958 (4)	0·4225 (5)	−0·0067 (3)	3·4 (1)
C(15)	0·1769 (5)	0·5509 (6)	0·0341 (4)	4·1 (1)
C(16)	0·1095 (4)	0·6486 (5)	−0·0102 (3)	4·0 (1)
C(17)	0·0604 (4)	0·6176 (6)	−0·0936 (4)	3·9 (1)
C(18)	0·0784 (4)	0·4891 (6)	−0·1346 (3)	3·33 (9)

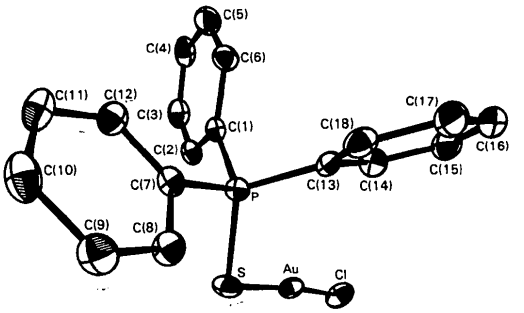

Fig. 1. Perspective view of the [(Ph_3PS)AuCl] molecule.

This elongation is probably a result of hydrophobic shielding by the Ph_3P moiety combined with a strong electron-withdrawing influence of the electronegative S atom in [(Ph_3PS)AuCl] as compared to the latter effect alone in the case of other S-bonded complexes such as [(PrImt)AuCl] or [(EtImt)AuCl] where PrImt and EtImt are *N*-propyl- or *N*-ethylimidazolidine-2-thione. The Au—Cl distance is the longest observed in linear gold(I) complexes. A still longer Au—Cl bond length, 2·818 Å in three-coordinate [(P—P)AuCl] and 2·771 Å in the dimeric [({(Ph_2P)$_2$}$_2$$CH_2$AuCl)$_2$], has been observed but only in nonlinear complexes or when the Cl ligand is bridging rather than terminal (Schmidbaur, Wohlenbau, Schubert, Frank & Huttner, 1977; Barrow, Burgi, Johnson & Venanzi, 1976).

The molecule shows a typical Au—S bond length of 2·256 (1) Å, consistent with other S donors coordinated *trans* to Cl. This Au—S length agrees with the average Au—S length of 2·26 Å in [$ClAuSCH_2Ph$]$_2$ (Drew & Riedl, 1973) and 2·262 and 2·271 Å in [Ph_4As]$^+$[Au(SPh)$_2$]$^-$ (Bates & Waters, 1985). It is slightly shorter than the Au—S length of 2·303–2·342 Å as seen in formally RS^- and S^{2-} complexes such as [Et_2PCH_2SAu]$_2$ (Crane & Beall, 1978) and [(Ph_3PAu)$_3$S]PF_6 (Jones, Sheldrick & Hadicke, 1980).

The geometry of the Ph_3P moiety is similar to that observed in other linear gold(I) complexes with triphenylphosphine as ligand (Jones, 1984, 1985). The average C—P—C and S—P—C angles are close to tetrahedral but the ligand has no overall tetrahedral or threefold symmetry, since the phenyl groups are not equivalently oriented around the P—S axis. The planes of the C(1)–C(6) and C(13)–C(18) phenyl rings intersect approximately along the P—S axis, while the plane of the C(7)–C(12) ring is perpendicular to the P—S bond. This is probably the most suitable packing avoiding any molecular constraints among the phenyl groups. All P—C and C—C distances and angles agree with the distances observed in other complexes.

Table 3. *Intramolecular bond distances* (Å) *and angles* (°)

Distances and angles involving Au, S, Cl and P atoms

Au—Cl	2·555 (1)	P—C(1)	1·797 (4)
Au—S	2·256 (1)	P—C(7)	1·802 (4)
S—P	2·017 (1)	P—C(13)	1·796 (4)
Au—S—P	106·35 (6)	P—C(1)—C(2)	121·1 (3)
Cl—Au—S	175·59 (5)	P—C(1)—C(6)	118·9 (3)
S—P—C(1)	113·7 (1)	P—C(7)—C(8)	117·7 (3)
S—P—C(7)	103·8 (1)	P—C(7)—C(12)	122·8 (3)
S—P—C(13)	114·6 (1)	P—C(13)—C(14)	118·4 (3)
C(1)—P—C(7)	109·3 (2)	P—C(13)—C(18)	123·1 (3)
C(1)—P—C(13)	106·4 (2)		
C(7)—P—C(13)	108·8 (2)		

Some non-bonded distances less than 3·8 Å

Au—S	3·695 (5)	Au—C(14)	3·576 (6)
S—C(14)	3·755 (5)	P—Au	3·424 (5)

Table 4. *A comparison of some important bond distances and angles of chloro(triphenylphosphine sulfide)gold*(I) *with related structures*

L = P, Se or S; PrImt and EtImt = *N*-propyl- and *N*-ethylimidazolidine-2-thiones.

	L—Au	L—Au—Cl	Au—Cl	Reference
[($PhO)_3$P)AuCl]	2·192 (5) Å	178·5 (2)°	2·273 (5) Å	(*a*)
[(Ph_3P)AuCl]	2·235 (3)	179·63 (8)	2·279 (3)	(*b*)
[(PrImt)AuCl]	2·25 (1)	172·5 (4)	2·27 (2)	(*c*)
[(EtImt)AuCl]	2·25 (1)	174·2 (3)	2·26 (1)	(*d*)
[(Ph_3PSe)AuCl]	2·371 (2)	178·6 (1)	2·277 (6)	(*e*)
[(Ph_3PS)AuCl]	2·256 (1)	175·59 (5)	2·555 (1)	(*f*)

(*a*) Hitchcock & Pye (1977); (*b*) Baenziger, Bennett & Soboroff (1967); (*c*) Hussain & Isab (1985); (*d*) Hussain & Isab (1984); (*e*) Hussain (1986); (*f*) present work.

The present crystal structure analysis is one of the few so far reported for stable water-soluble S–Au complexes with a significantly longer (hence weaker) Au–Cl bond length. Because of this weaker linkage the chloride should be easily replaced by other bonding sites in biological systems. Thus the title compound may prove to be another phosphine-based complex with anti-arthritic activity.

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Structure of a Neutral Uranium(IV)–Dipicolinic Acid Complex*†

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Abstract. Triaquabis(dipicolinato)uranium(IV) 3·5-hydrate, $[U(C_7H_3NO_4)_2(H_2O)_3].3{\cdot}5H_2O$, $M_r = 685{\cdot}34$, orthorhombic, $Pn2_1a$, $a = 9{\cdot}915$ (2), $b = 10{\cdot}280$ (2), $c = 20{\cdot}635$ (5) Å, $V = 2103{\cdot}25$ Å^3, $Z = 4$, $D_m = 2{\cdot}16$, $D_x = 2{\cdot}164$ Mg m^{-3}, λ(Mo $K\alpha_1$) = 0·70926 Å, $\mu = 7{\cdot}387$ mm^{-1}, $F(000) = 1300$, $T = 296$ K, $R = 0{\cdot}030$ for 1520 observed reflections. The structure consists of monomolecular units in which the U atom is nine-coordinated to four carboxylate O atoms, two pyridinic N atoms, and three O atoms of water molecules. The non-H atoms of each dipicolinato group are nearly coplanar, and the two groups of a given uranium polyhedron form a dihedral angle of 82 (2)° between them. Two of the interstitial water molecules are in ordered positions, while the remaining 1·5 molecules are distributed in three disordered positions with occupancies of about 0·5 each. The uranium polyhedra are interlinked by O—H···O hydrogen bonds between the water molecules in the structure.

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† Dipicolinic acid is pyridine-2,6-dicarboxylic acid.

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