Complexes with S-Donor Ligands. Part 2.[1] Synthesis of Anionic Bis(thiolato)gold(I) Complexes. Crystal Structure of $[N(PPh_3)_2][Au(SR)_2]$ (R = benzoxazol-2-yl)†

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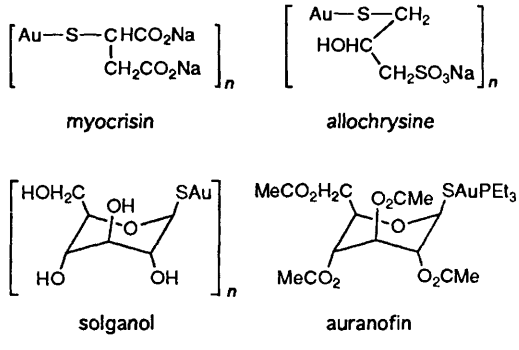
The reaction of $[N(PPh_3)_2][Au(acac)_2]$ (Hacac = acetylacetone) with HSR gave acetylacetone and the complexes $[N(PPh_3)_2][Au(SR)_2]$ [HSR = benzoxazole-2(1*H*)-thione **1**, pyrimidine-2(1*H*)-thione **2**, pyridine-2(1*H*)-thione **3**, 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose **4**, 2-thiouracil (2,3-dihydro-2-thioxo-1*H*-pyrimidin-4-one) **5**, 2,3-dihydro-1*H*-benzimidazole-2-thione **6**, 2-thiomalic acid **7**, 2-sulfanylethanol **8**, D-penicillamine (3-sulfanylvaline) **9**]. The crystal structure of **1** has been solved. The gold atom adopts the usual linear co-ordination [175.11(5)°] and the Au–S bond distances are normal [2.281(2) and 2.283(2) Å].

Interest in complexes containing Au–S bonds stems from their potential application in medicine (chrysotherapy)[2] and in the glass and ceramic industries.[3] Thus thiolatogold(I) complexes, such as the commercial antiarthritic drugs myocrisin, allochrysine, solganol or auranofin, are among the most important antiarthritic compounds.[2] In addition, solganol has *in vitro* inhibitory effects on Human Immunodeficiency Virus 1, which is the etiologic agent of AIDS,[4] and auranofin was found to be highly cytotoxic to tumour cells[5] and active against interperitoneal P388 leukemia.[6]

Most reported thiolatogold(I) complexes are of formula $[\{AuSR\}_n]$ or [Au(SR)L] (L = tertiary phosphine),[7] probably because of the importance of antiarthritic compounds and also because they are the easiest materials to obtain. Anionic $[Au(SR)_n]^{1-n}$ complexes are of interest because these species, where HSR is cysteine or glutathione [*N*-(*N*-L-γ-glutamyl-L-cysteinyl)glycine], are formed *in vivo* when myocrisin is injected.[8] However, very few $[Au(SR)_2]^-$ compounds are known (R = Ph,[9] Me, Bu^t,[9a] 2,4,6-$Pr^i_3C_6H_2$,[7h] C_6F_5[10] or 2,3,4,6-tetra-*O*-acetyl-1-β-D-glucopyranosyl[11]). These complexes have been obtained by treating the corresponding alkalimetal or ammonium thiolate with $[AuX_2]^-$ (X = Cl or Br),[9a,11] AuI[7h] or $[AuCl_4]^-$;[10] however, reported yields were low (35–38%).[10,11] In this paper we report a simple and direct method for good to high yield synthesis of $[N(PPh_3)_2][Au(SR)_2]$ complexes, starting from $[N(PPh_3)_2][Au(acac)_2]$ (Hacac = acetylacetone). One of the complexes (R = 2-pyridyl) and the method of synthesis were reported in a preliminary communication.[12]

Results and Discussion

All complexes reported in this paper were prepared following the acid–base reaction (1) where Hacac = acetylacetone and the moieties SR are shown in Table 1. The reactions leading to complexes **1**–**5** and **9** were carried out in dichloromethane using a 1:2 molar ratio of the reagents (see Table 1). The corresponding tetrabutylammonium salt of **4** has previously been reported in low yield (38%).[11] Other gold(I) derivatives of 2,3-dihydro-1*H*-benzimidazole-2-thione,[7m] pyrimidine-2(1*H*)-thione, pyridine-2(1*H*)-thione,[7m,t] 2-thiomalic acid,[7d] 2-thiouracil (2,3-dihydro-2-thioxo-1*H*-pyrimidin-4-one),[7l] and D-penicillamine (3-sulfanylvaline)[7a] have been reported.



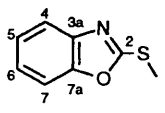
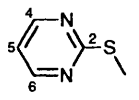
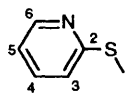
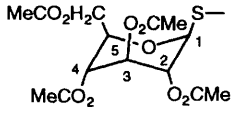
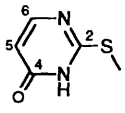
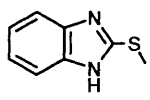
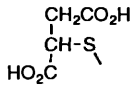
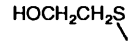
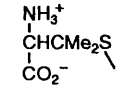
$$[N(PPh_3)_2][Au(acac)_2] + 2HSR \longrightarrow [N(PPh_3)_2][Au(SR)_2] + 2\ Hacac \quad (1)$$

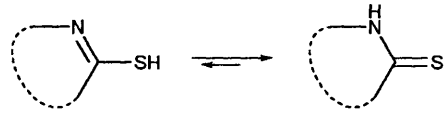
The synthesis of complexes **6**–**8** was carried out in acetone using an excess of the corresponding thiol. The use of dichloromethane as solvent or of a stoichiometric amount of the thiol leads to the formation of other products. Thus, the synthesis of **7** requires the slow addition of an acetone solution of $[N(PPh_3)_2][Au(acac)_2]$ to an acetone solution containing an excess (50%) of 2-thiomalic acid. If the gold complex is added as a solid to the acetone solution of the thiol, thus allowing a local excess of the complex, two different products were obtained. One of them, insoluble in all common solvents, was probably $[Au\{SCH(CH_2CO_2H)(CO_2H)\}]_n$ (by elemental analyses). The synthesis of **7** using dichloromethane as solvent was not possible, because of the low solubility of 2-thiomalic acid, which prevents an excess of the thiol. In addition, **7** decomposes rapidly in dichloromethane and slowly in acetone to give an insoluble, unidentified compound. If the reaction with 2-sulfanylethanol to give **8** is carried out in dichloromethane,

† In memory of our friend and colleague Professor Marisa Tiripicchio-Camellini.

Supplementary data available: Full details have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD 400955.

Table 1 The $[Au(SR)_2]^-$ complexes **1–9**

Complex	SR	HSR
1		benzoxazole-2(1*H*)-thione
2		pyrimidine-2(1*H*)-thione
3		pyridine-2(1*H*)-thione
4		2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose
5		2-thiouracil
6		2,3-dihydro-1*H*-benzimidazole-2-thione
7		2-thiomalic acid
8		2-sulfanylethanol
9		D-penicillamine



Scheme 1

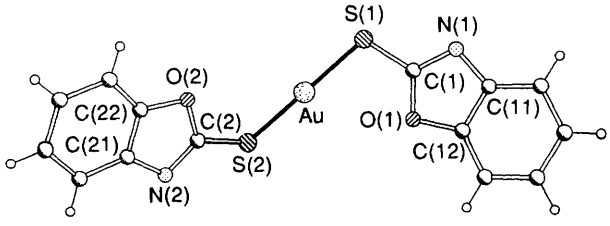


Fig. 1 Structure of the anion of complex **1**

$[Au(SCH_2CH_2OH)]_n$ is obtained as a by-product. In this case, because the thiol is soluble in dichloromethane, the problem is not the deficiency of the thiol but the instability of complex **8** in dichloromethane probably due to a dissociation equilibrium between **8** and $[Au(SCH_2CH_2OH)]_n$ plus $[N(PPh_3)_2][SCH_2CH_2OH]$. In fact, solutions of **8** in dichloromethane rapidly decompose to give $[Au(SCH_2CH_2OH)]_n$ (60% yield). Decomposition is slower in acetone but this solvent prevents recrystallization.

The acidities of thiols vary from that of phenol ($pK_a \approx 10$) to those of carboxylic acids,[13] which, together with the basic character of the N atom in the ligands benzoxazole-2(1*H*)-thione, pyrimidine-2(1*H*)-thione, pyridine-2(1*H*)-thione, 2-thiouracil and 2,3-dihydro-1*H*-benzimidazole-2-thione, implies the presence of both thiol and thione forms of these ligands in solution (see Scheme 1), although in the solid state the thione form is preferred.[7n,14] The corresponding deprotonated ligands can co-ordinate through the N and/or the S atoms.[15] However, because of the greater affinity of gold(I) for S rather than N donors, all reported complexes with this type of ligand are S-bonded.[7l–n,t,u]

The bands assignable to the ν(NH) mode in the IR spectra of benzoxazole-2(1*H*)-thione, pyrimidine-2(1*H*)-thione and pyridine-2(1*H*)-thione in the 3000–3330 cm^{-1} region are absent in complexes **1–3**. In unco-ordinated 2-thiouracil a strong band at 1702 cm^{-1} is assigned to ν(C=O).[16] In complex **5** this band is shifted to 1641 cm^{-1}. A similar decrease has been reported for the complex $[Au(SC_4N_2OH_3)(PPh_3)]$, the crystal structure of which shows S–Au co-ordination.[7l] The presence of several weak bands in the region in which ν(Au–S) has been assigned {250–350 cm^{-1} in $[Au(SR)_2]^-$ where R = Me or Bu^t[9]} makes the assignment of this band in our complexes difficult. The equivalence of protons and carbons 4 and 6 in the ^1H and ^{13}C NMR spectra of complex **2** confirms the S-co-ordination of the pyrimidine-2-thionato ligand.

The gold atom in complex **1** (see Table 2, Fig. 1) is linearly co-ordinated by two S atoms [S–Au–S 175.11(5)°] at distances [2.281(2), 2.283(2) Å] similar to those reported for other anionic thiolato complexes [R = Ph, 2.271(8), 2.262(8) Å;[9b] R = $C_6H_2Pr^i_3$, 2.288(4) Å[7h]], The C–S bond distances [1.715(6), 1.725(5) Å] are as expected for a $C(sp^2)$–S single bond, *cf.* the mean value of 1.712 Å in thiophenes.[17] The other distances are consistent with the bond orders indicated in Table 1 for the benzoxazole-2-thionato ligand. Both ligands are planar (mean deviation < 0.01 Å); their mutual orientation is indicated by the torsion angle C(1)–S(1) · · · S(2)–C(2) 108°.

Experimental

The IR spectra, elemental analyses, conductance measurements in acetone and melting-point determinations were carried out as described elsewhere.[18] The ^1H NMR spectra were recorded on Varian Unity-300 or Bruker AC-200 spectrometers, ^{13}C spectra on a Varian Unity-300 spectrometer using the same solvent and internal reference ($SiMe_4$). Carbon-13 NMR resonances of $[N(PPh_3)_2]^+$ appear, with little differences among complexes **1–9**, at δ 127 (dd of an AA′ system, J_{CP} = 108 and 0.8 Hz, *ipso*-C), 130 (m, *ortho*-C), 132 (m, *meta*-C) and 134 (s, *para*-C) and are not given below. The atom numbering is shown in Table 1. Complexes **6** and **8** were not soluble enough to record their NMR spectra.

Reactions were carried out at room temperature under nitrogen. $[N(PPh_3)_2][Au(acac)_2]$ was prepared according to literature methods;[12] benzoxazole-2-(1*H*)-thione, pyrimidine-2(1*H*)-thione, pyridine-2(1*H*)-thione, 2-thiouracil, 2,3-dihydro-1*H*-benzimidazole-2-thione, 2-thiomalic acid, 2-sulfanyl-

Table 2 Selected bond lengths (Å) and angles (°) for compound **1**

Au–S(2)	2.281(2)	Au–S(1)	2.283(2)
S(1)–C(1)	1.715(6)	C(1)–N(1)	1.318(7)
C(1)–O(1)	1.357(6)	N(1)–C(11)	1.384(7)
O(1)–C(12)	1.405(6)	S(2)–C(2)	1.725(5)
C(2)–N(2)	1.305(6)	C(2)–O(2)	1.381(6)
N(2)–C(21)	1.403(6)	O(22)–C(22)	1.397(6)
S(2)–Au–S(1)	175.11(5)	C(1)–S(1)–Au	106.8(2)
N(1)–C(1)–O(1)	114.2(5)	N(1)–C(1)–S(1)	122.1(4)
O(1)–C(1)–S(1)	123.7(4)	C(1)–N(1)–C(11)	105.7(4)
C(1)–O(1)–C(12)	104.0(4)	C(2)–S(2)–Au	107.5(2)
N(2)–C(2)–O(2)	115.4(4)	N(2)–C(2)–S(2)	124.4(4)
O(2)–C(2)–S(2)	120.2(4)	C(2)–N(2)–C(21)	103.9(4)
C(2)–O(2)–C(22)	103.5(4)		

ethanol, D-penicillamine (Fluka) and 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (Aldrich) were used as received.

Syntheses.—*Bis(triphenylphosphoranylidene)ammonium bis(benzoxazole-2-thionato)aurate*(I) **1**. Solid $[N(PPh_3)_2][Au(acac)_2]$ (129 mg, 0.14 mmol) was added to a solution of benzoxazole-2(1*H*)-thione (42 mg, 0.28 mmol) in dichloromethane (10 cm^3). The resulting solution was stirred for 2 h, filtered over anhydrous $MgSO_4$ and concentrated (3 cm^3). Addition of diethyl ether (15 cm^3) gave a white precipitate which was filtered off. The product was recrystallized from dichloromethane–diethyl ether and dried under vacuum. Yield 89%, m.p. 187 °C (Found: C, 57.70; H, 3.65; Au, 19.65; N, 4.05; S, 6.00. Calc. for $C_{50}H_{38}AuN_3O_2P_2S_2$: C, 57.95; H, 3.70; Au, 19.00; N, 4.05; S, 6.20%); Λ_M = 87 Ω^{-1} cm^2 mol^{-1} (5.1 × 10^{-4} mol dm^{-3}). NMR: ^1H (300 MHz, $CDCl_3$), δ 6.99 (td, 2 H, H^5, $^3J_{56}$ = $^3J_{54}$ = 7.5, $^4J_{57}$ = 1.4), 7.07 (td, 2 H, H^6, $^3J_{67}$ = 7.5, $^4J_{46}$ = 1.4 Hz), 7.20 [dm, 2 H, H^4], 7.3–7.7 [m, 32 H, $N(PPh_3)_2$ + H^7]; ^{13}C, δ 109.0, 117.0, 121.7 and 122.8 (C^4–C^7), 144.2 (C^{3a}), 151.9 (C^{7a}), 172.0 (C^2).

Bis(triphenylphosphoranylidene)ammonium bis(pyrimidine-2-thionato)aurate(I) **2**. Solid $[N(PPh_3)_2][Au(acac)_2]$ (133 mg, 0.14 mmol) was added to a solution of pyrimidine-2(1*H*)-thione (32 mg, 0.28 mmol) in dichloromethane (8 cm^3) to give a yellow solution which was stirred for 1.5 h. The resulting colourless solution was filtered over anhydrous $MgSO_4$ and concentrated (3 cm^3). Addition of diethyl ether (15 cm^3) gave a white precipitate which was filtered off and air dried. The product was recrystallized from dichloromethane–diethyl ether and acetone–diethyl ether. Yield 80%, m.p. 191 °C (Found: C, 55.15; H, 3.80; Au, 19.75; N, 7.25; S, 6.55. Calc. for $C_{44}H_{36}AuN_5P_2S_2$: C, 55.15; H, 3.80; Au, 20.55; N, 7.30; S, 6.70%). Λ_M = 92 Ω^{-1} cm^2 mol^{-1} (4.7 × 10^{-4} mol dm^{-3}). NMR: ^1H (200 MHz, $CDCl_3$), δ 6.62 (t, 2 H, H^5, $^3J_{HH}$ = 4.8 Hz), 7.3–7.7 [m, 30 H, $N(PPh_3)_2$], 8.27 (d, 4 H, H^4 and H^6); ^{13}C, δ 114.0 (C^5), 156.4 (C^4 and C^6), 181.4 (C^2).

Bis(triphenylphosphoranylidene)ammonium bis(pyridine-2-thionato)aurate(I) **3**. Pyridine-2(1*H*)-thione (24 mg, 0.22 mmol) was added to a solution of $[N(PPh_3)_2][Au(acac)_2]$ (101 mg, 0.11 mmol) in dichloromethane (10 cm^3) and the solution stirred overnight. The resulting solution was concentrated (2 cm^3) and diethyl ether (20 cm^3) added to precipitate a white solid which was filtered off and recrystallized from dichloromethane–diethyl ether to give **3**. Yield 87%, m.p. 190 °C (Found: C, 57.60; H, 4.00; Au, 21.10; N, 4.30; S, 7.20. Calc. for $C_{46}H_{38}AuN_3P_2S_2$: C, 57.80; H, 4.00; Au, 20.60; N, 4.40; S, 6.70%). Λ_M = 95 Ω^{-1} cm^2 mol^{-1} (5.4 × 10^{-4} mol dm^{-3}). NMR: ^1H (200 MHz, $CDCl_3$), δ 6.59 (dd, 2 H, H^5, $^3J_{HH}$ = 5, $^3J_{HH}$ = 8), 7.10 (t, 2 H, H^4, $^3J_{HH}$ = 8 Hz), 7.3–7.7 [m, 30 H, $N(PPh_3)_2$], 7.91 (d, 2 H, H^3), 8.12 (d, 2 H, H^6); ^{13}C, δ 116.4, 127.8 and 134.1 (C^{3-5}), 148.4 (C^6), 169.4 (C^2).

Bis(triphenylphosphoranylidene)ammonium bis(2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranosato-S)aurate(I) **4**. Solid $[N(PPh_3)_2][Au(acac)_2]$ (120 mg, 0.13 mmol) was added to a solution of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (96 mg, 0.26 mmol) in dichloromethane (10 cm^3). The resulting colourless solution was stirred for 2 h and filtered over anhydrous $MgSO_4$. The solvent was evaporated to dryness and the remaining residue was stirred with *n*-hexane until a white solid separated. The product was filtered off and dried *in vacuo*. Yield 75%, m.p. 85 °C (Found: C, 52.25; H, 4.60; Au, 14.00; N, 1.15; S, 4.30. Calc. for $C_{64}H_{70}AuNO_{18}P_2S_2$: C, 52.55; H, 4.80; Au, 13.45; N, 0.95; S, 4.40%). Λ_M = 50 Ω^{-1} cm^2 mol^{-1} (2.4 × 10^{-4} mol dm^{-3}). NMR: ^1H (200 MHz, $CDCl_3$), δ 1.97, 1.99, 2.02 and 2.09 (s, 24 H, COMe), 3.70–3.74 (m, 2 H, H^5), 4.05–4.26 (m, 4 H, CH_2), 4.90–5.30 (m, 8 H, H^1–H^4); ^{13}C, δ 20.79, 20.87, 21.00, 21.59 (Me), 63.03, 63.33, 75.02, 75.38, 76.60, 82.92 (CH_2, C^1–C^5), 169.65, 169.94, 170.54 and 171.16 (CO).

Bis(triphenylphosphoranylidene)ammonium bis(2-thiouracilato-S)aurate(I) **5**. Solid $[N(PPh_3)_2][Au(acac)_2]$ (155 mg, 0.16 mmol) was added to a suspension of 2-thiouracil (43 mg, 0.34 mmol) in dichloromethane (8 cm^3). On stirring the suspension for 2 h dissolution of the thiol was observed. The solution was filtered over anhydrous $MgSO_4$ and concentrated (3 cm^3). Addition of diethyl ether (15 cm^3) gave a white precipitate which was filtered off and air dried. The product was recrystallized from dichloromethane–diethyl ether. Yield 88%, m.p. 197 °C (Found: C, 53.35; H, 3.70; Au, 20.50; N, 7.00; S, 6.35. Calc. for $C_{44}H_{36}AuN_5O_2P_2S_2$: C, 53.40; H, 3.65; Au, 19.90; N, 7.10; S, 6.50%). Λ_M = 89 Ω^{-1} cm^2 mol^{-1} (4.9 × 10^{-4} mol dm^{-3}). NMR: ^1H (300 MHz, $CDCl_3$), δ 5.95 (d, 2 H, H^5, $^3J_{HH}$ = 6.3 Hz), 7.3–7.7 [m, 30 H, $N(PPh_3)_2$], 7.84 (d, 2 H, H^6), 10.4 (br, 2 H); ^{13}C, δ 108.6 (C^5), 155.5 (C^6), 163.3 (C^4), 170.5 (C^2).

Bis(triphenylphosphoranylidene)ammonium bis(benzimidazole-2-thionato)aurate(I) **6**. Solid $[N(PPh_3)_2][Au(acac)_2]$ (158 mg, 0.17 mmol) was added to a solution of 2,3-dihydro-1*H*-benzimidazole-2-thione (76 mg, 0.51 mmol) in acetone (10 cm^3). The resulting colourless solution was stirred for 2.5 h, filtered over anhydrous $MgSO_4$ and concentrated until a small amount of **6** precipitated (3 cm^3). Excess of 2,3-dihydro-1*H*-benzimidazole-2-thione was precipitated by addition of dichloromethane (10 cm^3) and removed by filtration. The filtrate was concentrated (2 cm^3) and diethyl ether (15 cm^3) added to complete the precipitation of **6**. The product was recrystallized from dichloromethane–diethyl ether and acetone–diethyl ether, and dried *in vacuo*. Yield 81%, m.p. 173 °C (Found: C, 57.90; H, 4.00; Au, 18.30; N, 6.50; S, 6.15. Calc. for $C_{50}H_{40}AuN_5P_2S_2$: C, 58.10; H, 3.90; Au, 19.05; N, 6.75; S, 6.20%). Λ_M = 71 Ω^{-1} cm^2 mol^{-1} (1.3 × 10^{-4} mol dm^{-3}).

Bis(triphenylphosphoranylidene)ammonium bis(2-thiomalato-S)aurate(I) **7**. A solution of $[N(PPh_3)_2][Au(acac)_2]$ (173 mg, 0.19 mmol) in acetone (10 cm^3) was added dropwise to a stirring solution of 2-thiomalic acid (84 mg, 0.56 mmol) in acetone (4 cm^3). The resulting colourless solution was stirred for 2 h and then filtered over Celite and concentrated (3 cm^3). Addition of diethyl ether (15 cm^3) gave a white precipitate which was collected by filtration under a nitrogen atmosphere. The product was recrystallized from acetone–diethyl ether and dried *in vacuo*. Yield 81%, m.p. 91 °C (Found: C, 51.45; H, 4.00; Au, 19.40; N, 1.40; S, 5.50. Calc. for $C_{44}H_{40}AuN_2O_2P_2S_2$: C, 51.10; H, 3.90; Au, 19.05; N, 1.35; S, 6.20%). Λ_M = 95 Ω^{-1} cm^2 mol^{-1} (3.5 × 10^{-4} mol dm^{-3}). NMR: ^1H [200 MHz, $(CD_3)_2CO$], δ 2.84 [br, 2 H, H_A (CH_2)], 3.07 [br, 2 H, H_B (CH_2)], 4.01 (br, 2 H, CH), 5.35 (vbr, 4 H, CO_2H), 7.5–7.8 [m, 30 H, $N(PPh_3)_2$]; ^{13}C, δ 40.34, 44.59 (CH, CH_2), 173.7, 177.7 (CO_2H).

Bis(triphenylphosphoranylidene)ammonium bis(1-hydroxyethane-2-thiolato)aurate(I) **8**. A solution of $[N(PPh_3)_2][Au(acac)_2]$ (120 mg, 0.13 mmol) in acetone was added dropwise to a stirring solution of 2-sulfanylethanol (27 μl, 30 mg, 0.39 mmol) in acetone (2 cm^3). The resulting colourless solution was stirred for 5 min, filtered over anhydrous $MgSO_4$ and concentrated (3 cm^3). Addition of diethyl ether (15 cm^3)

Table 3 Atomic coordinates ($\times 10^4$) for compound **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au	6 442.67(8)	5 324.3(2)	1 118.77(7)	C(41)	4 176(2)	6 936(4)	1 786(2)
S(1)	6 943.3(6)	6 666.4(11)	879.8(5)	C(42)	4 124(2)	7 245(4)	2 270(2)
C(1)	7 140(2)	7 398(4)	1 396(2)	C(43)	4 172(2)	6 530(4)	2 644(2)
N(1)	7 428(2)	8 249(3)	1 381(2)	C(44)	4 279(2)	5 530(4)	2 552(2)
O(1)	7 018.4(14)	7 159(3)	1 850.3(13)	C(45)	4 340(2)	5 230(4)	2 079(2)
C(11)	7 522(2)	8 607(4)	1 861(2)	C(46)	4 290(2)	5 929(4)	1 701(2)
C(12)	7 268(2)	7 947(4)	2 155(2)	C(51)	3 260(2)	7 556(4)	1 041(2)
C(13)	7 293(2)	8 076(5)	2 657(2)	C(52)	2 882(2)	8 349(5)	900(2)
C(14)	7 585(2)	8 923(5)	2 858(2)	C(53)	2 318(2)	8 125(5)	708(2)
C(15)	7 832(2)	9 594(5)	2 570(2)	C(54)	2 144(2)	7 142(5)	662(2)
C(16)	7 806(2)	9 459(4)	2 066(2)	C(55)	2 513(2)	6 351(6)	791(2)
S(2)	6 005.6(6)	3 897.2(11)	1 346.5(5)	C(56)	3 076(2)	6 566(5)	983(2)
C(2)	5 291(2)	4 007(4)	1 123(2)	C(61)	5 052(2)	10 099(4)	1 448(2)
N(2)	4 890(2)	3 532(3)	1 306(2)	C(62)	5 376(2)	9 346(4)	1 716(2)
O(2)	5 111.8(14)	4 600(3)	712.7(12)	C(63)	5 968(2)	9 383(4)	1 769(2)
C(21)	4 392(2)	3 807(4)	991(2)	C(64)	6 226(2)	10 186(5)	1 568(2)
C(22)	4 525(2)	4 452(4)	629(2)	C(65)	5 909(2)	10 953(4)	1 316(2)
C(23)	4 135(2)	4 850(4)	263(2)	C(66)	5 318(2)	10 901(4)	1 253(2)
C(24)	3 576(2)	4 584(4)	272(2)	C(71)	4 056(2)	10 874(4)	1 824(2)
C(25)	3 423(2)	3 946(4)	636(2)	C(72)	3 538(2)	10 697(4)	1 985(2)
C(26)	3 825(2)	3 546(4)	1 006(2)	C(73)	3 345(2)	11 339(4)	2 320(2)
P(1)	3 995.0(5)	7 816.1(9)	1 291.3(4)	C(74)	3 674(2)	12 157(4)	2 504(2)
P(2)	4 288.2(5)	10 019.3(9)	1 386.5(4)	C(75)	4 188(2)	12 339(4)	2 357(2)
N(3)	4 066(2)	8 927(3)	1 506.7(14)	C(76)	4 382(2)	11 701(4)	2 014(2)
C(31)	4 411(2)	7 537(4)	811(2)	C(81)	4 016(2)	10 446(4)	770(2)
C(32)	4 991(2)	7 381(4)	926(2)	C(82)	3 510(2)	10 996(4)	675(2)
C(33)	5 322(2)	7 319(5)	548(2)	C(83)	3 274(2)	11 216(4)	194(2)
C(34)	5 076(2)	7 421(4)	66(2)	C(84)	3 533(2)	10 901(4)	−196(2)
C(35)	4 502(2)	7 538(4)	−53(2)	C(85)	4 032(2)	10 352(4)	−105(2)
C(36)	4 169(2)	7 604(4)	319(2)	C(86)	4 274(2)	10 125(4)	372(2)

gave a white precipitate which was filtered off and dried *in vacuo*. Yield 70%, m.p. 117 °C (Found: C, 53.50; H, 4.65; Au, 22.20; N, 1.65; S, 7.45. Calc. for $C_{40}H_{40}AuNO_2P_2S_2$: C, 54.00: H, 4.50; Au, 22.15; N, 1.55; S, 7.20%). Λ_M = 94 Ω^{-1} cm^2 mol^{-1} (2.4×10^{-4} mol dm^{-3}).

*Bis(triphenylphosphoranylidene)ammonium bis(*D*-penicillaminato-*S*)aurate*(I) **9**. A solution of $[N(PPh_3)_2][Au(acac)_2]$ (130 mg, 0.14 mmol) was added dropwise to a stirring suspension of D-penicillamine (42 mg, 0.28 mmol) in dichloromethane (2 cm^3). On stirring for 1 h the thiol dissolved. The solution was filtered over Celite and concentrated (3 cm^3). Addition of diethyl ether (15 cm^3) gave a white precipitate which was filtered off. The product was recrystallized from dichloromethane–diethyl ether and dried *in vacuo*. Yield 95%, m.p. 138 °C (Found: C, 53.00; H, 4.95; Au, 20.20; N, 3.80; S, 5.70. Calc. for $C_{46}H_{50}AuN_3O_4P_2S_2$: C, 53.55; H, 4.90; Au, 19.10; N, 4.05; S, 6.20%). Λ_M = 85 Ω^{-1} cm^2 mol^{-1} (4.4×10^{-4} mol dm^{-3}). NMR: ^{1}H (300 MHz, CD_2Cl_2), δ 1.22 (s, 6 H, Me), 1.62 (s, 6 H, Me), 3.61 (s, br, 2 H), 7.47–7.69 [m, $N(PPh_3)_2$]; ^{13}C, δ 30.00 (Me), 36.09 (Me), 47.74 (CS), 66.94 (CH), 171.42 (CO_2H).

X-Ray Structure Determination of Compound **1**.—*Crystal data*. $C_{50}H_{38}AuN_3O_2P_2S_2$, M_r = 1035.86, monoclinic, space group *C*2/*c*, *a* = 23.834(7), *b* = 13.170(4), *c* = 27.379(9) Å, β = 98.76(3)°, *U* = 8493 Å^3, *Z* = 8, D_c = 1.620 Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ = 3.7 mm^{-1}, *F*(000) = 4128, *T* = −100 °C.

Data collection and reduction. A colourless prism *ca.* 0.4 × 0.3 × 0.2 mm was mounted in inert oil (type RS3000, donated by Riedel de Haën) on a glass fibre and transferred to the cold-gas stream of the diffractometer (Siemens R3 with LT-2 low-temperature attachment). A total of 10 048 intensities was registered to $2\theta_{max}$ 50°. Absorption corrections were based on ψ scans, with transmissions 0.70–0.95, after which 7516 reflections were independent (R_{int} 0.024). Cell constants were refined from setting angles of 50 reflections in the range 2θ 20–23°.

Structure solution and refinement. The structure was solved by the heavy-atom method and refined[19] anisotropically on F^2 to $wR(F^2)$ 0.082, conventional $R(F)$ 0.032. Hydrogen atoms were included using a riding model. 541 Parameters; 466 restraints to light-atom thermal parameters; *S* 1.05; max. Δρ 1.2 e Å^{-3}. The assignment of the O and N atoms of the heterocycles was based mainly on the short C–N bonds, but also on the more regular *U* values; differences in *R* values on exchanging O and N atoms were marginal. Final atomic coordinates are presented in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank Dirección General de Investigación Científica y Técnica (PB92-0982-C) and the Fonds der Chemischen Industrie for financial support. P. G.-H. thanks Fundación Cultural Caja de Ahorros del Mediterraneo for a grant.

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Received 22*nd April* 1994; *Paper* 4/02384F