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Au–O Interactions and others in triphenylphosphinegold(I) sulfanylpropenoates with diverse structures

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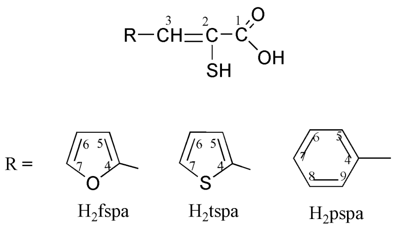
We investigated the reactions of triphenylphosphinegold(I) chloride in ethanol or methanol with the 3-(2-aryl)-2-sulfanylpropenoic acids H_2xspa [x = f, t, p; f = 3-(2-furyl)-, t = 3-(2-thienyl)-, p = 3-phenyl-; spa = 2-sulfanylpropenoato] in 1 : 1 and 2 : 1 mole ratios, and the reactions of diisopropylamine with the 1 : 1 complexes. Compounds of types [Au(PPh_3)(Hxspa)], [HQ][Au(PPh_3)(xspa)] (HQ = diisopropylammonium) and [($AuPPh_3$)$_2$(xspa)] were isolated and characterized by IR, Raman and FAB mass spectrometry and by ^1H, ^{13}C and ^{31}P NMR spectroscopy. The structures of (Htspa)$_2$·Me_2CO and of the complexes [Au(PPh_3)(Hfspa)] (**1**), [HQ][Au(PPh_3)(pspa)] (**6**), [($AuPPh_3$)$_2$(fspa)] (**7**), [($AuPPh_3$)$_2$(tspa)]·2MeOH (**8**·2MeOH) and [($AuPPh_3$)$_2$pspa]·2MeOH (**9**·2MeOH) were determined by X-ray diffractometry; those of the Au complexes exhibit π-stacking, hydrogen bonding and Au–Au and Au–O interactions as well as the expected Au–S and Au–P bonds.

Introduction

Well-known for their antiarthritic properties, Au(I) complexes [AuLX] that contain both thiolate and phosphine ligands have also attracted interest as potential antitumour agents.[1] Since the susceptibility of the thiolate to replacement by biological ligands is presumed to modulate the biological activity of these compounds,[2] it is attractive to explore the activities of members of this family in which the S–Au bond has been stabilized by endowing the thiolate ligand with other groups that are also capable of binding to the metal. In particular, Au ··· O interactions may be sought by using sulfanylcarboxylates. Although no significant Au ··· O interactions have been found when sulfanylalkanoates or sulfanyl benzoates have been used (at least when the phosphine ligand is triphenylphosphine),[2b,3–6] the observation[7] that in triorganotin(IV) complexes of arylsulfanylpropenoates the Sn–O distances are shorter than in a related sulfanylethanoate complex has suggested to us that Au–O interactions might be found in Au(PPh_3) complexes of arylsulfanylpropenoates.

In the solid state, many [AuLX] compounds are known to aggregate through intermolecular Au ··· Au or Au ··· S interactions, but if L or X has additional bonding capabilities, as in the case of triphenylphosphinegold(I) sulfanylcarboxylates, hydrogen bonding, van der Waals forces and/or other interactions can broaden the range of possible structures considerably.[3] In [Au(PPh_3)(SCH(Me)CO_2H)][2b] and [Au(PPh_3)-(SC$Me_2$$CO_2$H)],[4] in which the gold atom is coordinated to the S and P atoms in an essentially linear P–Au–S unit, a hydrogen bond between the carboxyl group and a neighbouring molecule gives rise to a dimer. In [Au(PPh_3)(SCH_2CO_2H)][4] an Au ··· S interaction between neighbouring molecules and a hydrogen bond between CO_2H groups together give rise to a polymeric network. [Au(PPh_3)(6-Hmna)][2b] (6-H_2mna = 6-sulfanylnicotinic acid) has a polymeric network based on π–π stacking and hydrogen bonding. We hypothesized that the use of sulfanylpropenoates might lead to a variety of structures which, given the possibility of deprotonation of both the sulfanyl and carboxyl groups,[7,8] might include interesting dinuclear complexes with Au–Au bonds.[9] The only previous report of plurinuclear Au(I)-phosphine complexes of sulfanylcarboxylates concerned the tetrafluoroborates of the cationic complexes [($AuPPh_3$)$_2$-$SCH_2C(O)OAu(PPh_3)$]$^+$ and [($AuPPh_3$)$_2$$SC_6H_4CO_2H$]$^+$.[10]

Here we describe the products of the reactions of Au(PPh_3)Cl in 1 : 1 and 2 : 1 mole ratios with the arylsulfanylpropenoic acids depicted in Scheme 1, and of the reactions of the 1 : 1 complexes so prepared with diisopropylamine. The aryl groups R in Scheme 1 were chosen both on account of the possibility of their engaging in intermolecular interactions, and because of their likely influence on the hydrophilicity and lipophilicity of the complexes prepared, which are of great importance for drug action.[1,2] Five of the new complexes {[Au(PPh_3)(Hfspa)] (**1**), [HQ][Au(PPh_3)(pspa)] (**6**) ([HQ] = diisopropylammonium), [($AuPPh_3$)$_2$(fspa)] (**7**), [($AuPPh_3$)$_2$(tspa)]·2MeOH (**8**·2MeOH) and [($AuPPh_3$)$_2$(pspa)]·2MeOH (**9**·2MeOH)} were isolated as single crystals, the structures of which, elucidated by X-ray crystallography, were found to feature π-stacking, hydrogen bonding, Au–Au and Au–O interactions as well as Au–S and Au–P bonds. We also describe the crystal structure of (Htspa)$_2$·Me_2CO, which was isolated in an attempt to crystallize H_2tspa from acetone in air.



Scheme 1

Experimental

Material and methods

The 3-(2-aryl)-2-sulfanylpropenoic acids H_2fspa, H_2tspa and H_2pspa were prepared[11] by condensation of the appropriate aldehyde with rhodanine, subsequent hydrolysis in an alkaline medium and acidification with aqueous HCl. Triphenylphosphinegold(I) chloride (Aldrich) and diisopropylamine (Merck) were used as supplied.

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Elemental analyses, melting points and IR, Raman and mass spectra (the data characterizing the metallated MS peaks were calculated for the isotope ^{197}Au) were obtained as in ref. 8. NMR spectra (^{1}H in dmso-d$_6$ and ^{13}C in dmso-d$_6$ or chloroform) were recorded at room temperature on a Bruker AMX 300 operating at 300.14 and 75.40 MHz, respectively, using 5 mm o.d. tubes; chemical shifts are reported relative to TMS using the solvent signal as reference (δ ^{1}H = 2.50 ppm; δ ^{13}C = 39.5 ppm). ^{31}P NMR spectra were recorded in chloroform at 202.46 MHz on a Bruker AMX 500 spectrometer using 5 mm o.d. tubes and are reported relative to external neat H_3PO_4 (85%).

Synthesis

The complexes of type $[Au(PPh_3)(Hxspa)]$ (x = f, t, p) were prepared by adding $Au(PPh_3)Cl$ in 1 : 1 mole ratio to a solution of the appropriate sulfanylcarboxylic acid and KOH in ethanol. After stirring at room temperature for 1 h, the ethanol was evaporated under vacuum and the solid formed was washed with water and dried *in vacuo*.

The complexes $[HQ][Au(PPh_3)(xspa)]$ (HQ = diisopropylammonium) were prepared by adding diisopropylamine to a solution of the appropriate 1 : 1 complex in ethanol. After stirring at room temperature for 24 h the ethanol was evaporated and the solid formed was dried *in vacuo*.

The complexes of type $[(AuPPh_3)_2(xspa)]$ were prepared by adding $Au(PPh_3)Cl$ in 2 : 1 mole ratio to a solution of the appropriate sulfanylcarboxylic acid and NaOH in methanol, or by adding $Au(PPh_3)Cl$ and NaOH to a solution of the appropriate 1 : 1 complex in methanol. After stirring and refluxing for 1 h, the methanol was evaporated and the solid formed was washed with water and dried *in vacuo*.

$[Au(PPh_3)(Hfspa)]$ (1). H_2fspa (0.034 g, 2.0 mmol), $Au(PPh_3)Cl$ (0.100 g, 2.0 mmol), ethanol (8 cm^3), KOH (0.011 g, 2.0 mmol), H_2O (2 cm^3), light brown solid. Yield: 83%. Mp 171 °C. Anal. Found: C 48.1, H 3.2, S 5.0. Calc. for $C_{25}H_{21}O_3SPAu$: C 47.8, H 3.0, S 5.1%. MS (FAB): the main metalated signals are at *m*/*z* 1409 (10%), $[(AuPPh_3)_3S]^+$ 1087 (82), $[(AuPPh_3)_2(fspa)]^+$; 721 (17), $[(PPh_3)_2Au]^+$; 628 (58), $[M]^+$; and 459 (100), $[(PPh_3)Au]^+$. IR (cm^{-1}): 1659vs, ν(C=O); 1435s, δ(OH); 1276m, ν(C–O); 1475m, 1435s, $\nu(PPh_3)$. NMR (DMSO-d$_6$): ^{1}H, δ 12.70 (s, br 1H, C(1)OH), 7.57 (s, 1H, C(3)H), 7.53 (d, 1H, C(5)H) 6.63 (t, 1H, C(6)H) 7.72 (d, 1H, C(7)H), 7.60 (m, 15H, H (Ph_3)); ^{13}C, δ 170.1 C(1), 123.4 C(2), 128.8 C(3), 152.4 C(4), 113.9 C(5), 112.2 C(6), 142.9 C(7); ^{31}P{^{1}H}, δ 35.6 (s). Single crystals were grown by slow evaporation of a solution in acetone.

$[Au(PPh_3)(Htspa)]\cdot H_2O$ ($2\cdot H_2O$). H_2tspa (0.034 g, 2.0 mmol), $Au(PPh_3)Cl$ (0.100 g, 2.0 mmol), ethanol (8 cm^3), KOH (0.011 g, 2.0 mmol), H_2O (2 cm^3), light brown solid. Yield: 89%. Mp 165 °C. Anal. Found: C 45.8, H 3.1, S 10.2. Calc. for $C_{25}H_{22}O_3S_2PAu$: C 45.3, H 3.3, S 9.7%. MS (FAB): the main metalated signals are at *m*/*z* 1409 (1%), $[(AuPPh_3)_3S]^+$; 1103 (1), $[(AuPPh_3)_2(tspa)]^+$; 721 (1), $[(PPh_3)_2Au]^+$; 644 (5), $[M]^+$; and 459 (10), $[(PPh_3)Au]^+$. IR (cm^{-1}): 1656vs, ν(C=O); 1436s, δ(OH); 1276s, ν(C–O); 1480m, 1436s, $\nu(PPh_3)$. NMR (DMSO-d$_6$): ^{1}H, δ 12.68 (s, br, 1H, C(1)OH), 7.98 (s, 1H, C(3)H), 7.45 (d, 1H, C(5)H) 7.13 (t, 1H, C(6)H), 7.59 (d, 1H, C(7)H), 7.56 (m, 15H, H (Ph_3)); ^{13}C, δ 170.1 C(1), 126.2 C(2), 131.6 C(3), 140.86 C(4), 131.5 C(5), 128.7 C(6), 130.2 C(7); ^{31}P{^{1}H}, δ 36.2 (s).

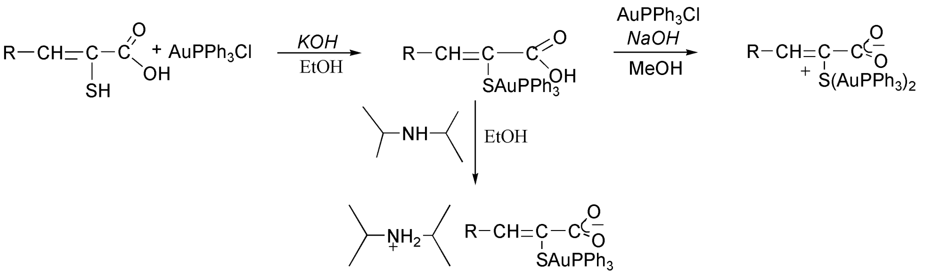
$[Au(PPh_3)(Hpspa)]$ (3). H_2pspa (0.036 g, 2.0 mmol), $Au(PPh_3)Cl$ (0.100 g 2.0 mmol), ethanol (8 cm^3), KOH (0.011 g, 2.0 mmol), H_2O (2 cm^3), light yellow solid. Yield: 84%. Mp 160 °C. Anal. Found: C 50.4, H 3.8, S 5.2. Calc. for $C_{27}H_{22}O_2SPAu$: C 50.8, H 3.5, S 5.0%. MS (FAB): the main metalated signals are at *m*/*z* 1409 (11%), $[(AuPPh_3)_3S]^+$; 1097 (82), $[(AuPPh_3)_2(pspa)]^+$; 721 (34), $[(PPh_3)_2Au]^+$; 638 (12), $[M]^+$; and 459 (100), $[(PPh_3)Au]^+$. IR (cm^{-1}): 1663s, ν(C=O); 1437vs, δ(OH); 1254m, ν(C–O); 1481m, 1437vs, $\nu(Ph_3P)$. NMR (DMSO-d$_6$): ^{1}H, δ 12.60 (s, 1H, C(1)OH), 7.51 (s, 1H, C(3)H), 8.10 (d, 2H, C(5)H$_o$) 7.36 (t, 2H, C(6)H$_m$), 7.22 (m, 1H, C(7)H$_p$), 7.60 (m, 15H, H(PPh_3)); ^{13}C, δ 171.1 C(1), 127.8 C(2), 136.5 C(3), 134.4 C(4), 130.3 C(5), 127.6 C(6), 128.6 C(7); ^{31}P{^{1}H}, δ 35.3 (s).

$[HQ][Au(PPh_3)(fspa)]$ (4). $[Au(PPh_3)(Hfspa)]$ (0.090 g, 14.3 mmol), diisopropylamine (0.020 cm^3), ethanol (15 cm^3), light brown solid. Yield: 48%. Mp 176 °C. Anal. Found: C 50.7, H 4.8, S 4.3, N 2.0. Calc. for $C_{31}H_{35}O_3SPAuN$: C 51.0, H 4.8, S 4.4, N 1.9%. MS (FAB): the main metalated signals are at *m*/*z* 1409 (30%), $[(AuPPh_3)_3S]^+$; 1087 (27), $[(AuPPh_3)_2(fspa)]^+$; 729 (5), $[M]^+$ 721 (11), $[(PPh_3)_2Au]^+$; 628 (44), $[Au(PPh_3)(fspa)]^+$; and 459 (100), $[(PPh_3)Au]^+$. IR and Raman (R) (cm^{-1}): 1614s, $\nu(NH_2^+)$; 1572s, 1581vs (R), $\nu_a(CO_2)$; 1340vs, $\nu_s(CO_2)$; 1481s, 1436s, 1481s (R), $\nu(PPh_3)$. NMR (DMSO-d$_6$): ^{1}H, δ 7.43 (s, 1H, C(3)H), 7.23 (d, 1H, C(5)H) 6.53 (m, 1H, C(6)H) 7.59 (d, 1H, C(7)H), 7.55 (m, 15H, H (Ph_3)), 1.12 (d, 12H, CH_3 [HQ]), 3.18 (m, 2H, CH [HQ]), 8.30 (s, 2H, NH_2^+ [HQ]); ^{13}C, δ 171.2 C(1), 119.1 C(2), 128.7 C(3), 154.1 C(4), 111.8 C(5), 110.5 C(6), 141.0 C(7), 45.6 CH [HQ], 19.7 CH_3 [HQ]; ^{31}P{^{1}H}, δ 36.16 (s).

$[HQ][Au(PPh_3)(tspa)]$ (5). $[Au(PPh_3)(Htspa)]$ (0.210 g, 32.0 mmol), diisopropylamine (0.046 cm^3), ethanol (30 cm^3), light brown solid. Yield 55%. Mp 160 °C. Anal. Found: C 49.3, H 4.4, S 7.9, N 1.6. Calc. for $C_{31}H_{35}O_2S_2PAuN$: C 49.9, H 4.7, S 8.6, N 1.9%. MS (FAB): the main metalated signals are at *m*/*z* 1409 (3%), $[(AuPPh_3)_3S]^+$; 1103 (4), $[(AuPPh_3)_2(tspa)]^+$; 721 (11), $[(PPh_3)_2Au]^+$; 644 (1), $[Au(PPh_3)(Htspa)]^+$; and 459 (20), $[(PPh_3)Au]^+$. IR (cm^{-1}): 1610s, $\nu(NH_2^+)$; 1560s, $\nu_a(CO_2)$; 1330vs, $\nu_s(CO_2)$; 1478s, 1436vs, $\nu(PPh_3)$. NMR (DMSO-d$_6$): ^{1}H, δ 7.89 (s, 1H, C(3)H), 7.30 (d, 1H, C(5)H) 7.08 (t, 1H, C(6)H), 7.65 (d, 1H, C(7)H), 7.56 (m, 15H, H (Ph_3)), 1.16 (d, 12H, CH_3 [HQ]), 2.23 (m, 2H, CH [HQ]), 8.31 (s, 2H, NH_2^+ [HQ]); ^{13}C, δ 172.3 C(1), 127.3 C(2), 134.8 C(3), 143.5 C(4), 133.4 C(5), 127.3 C(6), 131.2 C(7), 46.5 CH [HQ], 20.1 CH_3[HQ]; ^{31}P{^{1}H}, δ 35.27 (s).

$[HQ][Au(PPh_3)(pspa)]$ (6). $[Au(PPh_3)(Hpspa)]$ (0.100 g, 15.0 mmol), diisopropylamine (0.022 cm^3), ethanol (15 cm^3), white solid. Yield: 55%. Mp 85 °C. Anal. Found: C 53.3, H 5.0, S 4.6, N 1.7. Calc. for $C_{33}H_{37}O_2SPAuN$: C 53.0, H 5.0, S 4.3, N 1.9%. MS (FAB): the main metalated signals are at *m*/*z* 1409 (10%), $[(AuPPh_3)_3S]^+$; 1097 (59), $[(AuPPh_3)_2(ppa)]^+$; 740 (3), $[M]^+$; 721 (34), $[(PPh_3)_2Au]^+$; 638 (16), $[Au(PPh_3)(Hpspa)]^+$; and 459 (100), $[(PPh_3)Au]^+$. IR and Raman (R) (cm^{-1}): 1593s, $\nu(NH_2^+)$; 1552s, 1558vs (R), $\nu_a(CO_2)$; 1336s, $\nu_s(CO_2)$; 1480s, 1437vs, $\nu(PPh_3)$. NMR (DMSO-d$_6$): ^{1}H, δ 7.52 (s, 1H, C(3)H), 8.00 (d, 2H, C(5)H$_o$) 7.29 (t, 2H, C(6)H$_m$), 7.15 (m, 1H, C(7)H$_p$), 7.55 (m, 15H, H (PPh_3)), 1.12 (d, 12H, CH_3 [HQ]), 3.18 (m (overlapping), 2H, CH [HQ]), not observed (NH_2^+ [HQ]); ^{13}C, δ 171.8 C(1), 127.6 C(2), 137.9 C(3), 136.9 C(4), 130.3 C(5), 126.5 C(6), 128.9 C(7), 46.3 CH [HQ], 20.3 CH_3 [HQ]; ^{31}P{^{1}H}, δ 35.74 (s). Single crystals were grown by slow evaporation of acetone.

$[(AuPPh_3)_2(fspa)]\cdot H_2O$ ($7\cdot H_2O$). H_2fspa (0.026 g, 1.5 mmol), $Au(PPh_3)Cl$ (0.150 g, 3.0 mmol), methanol (12 cm^3), NaOH (0.012 g, 3.0 mmol), H_2O (3 cm^3), light brown solid. Yield: 64%. Mp 120 °C. Anal. Found: C 45.9, H 3.1, S 2.8. Calc. for $C_{43}H_{36}O_4SP_2Au_2$: C 46.7, H 3.1, S 2.9%. MS (FAB): the main metalated signals are at *m*/*z* 1409 (9%), $[(AuPPh_3)_3S]^+$; 1087 (100), $[M]^+$; 721 (71), $[(PPh_3)_2Au]^+$; 627 (5), $[Au(PPh_3)(Hfspa)]^+$; and 459 (94), $[(PPh_3)Au]^+$. IR and Raman (R) (cm^{-1}): 1581m, 1585m (R), ν_{as}(COO); 1478m, 1478m (R), 1436s, $\nu(Ph_3P)$. NMR (DMSO-d$_6$): ^{1}H, δ 7.44 (s, 1H, C(3)H), 7.20 (d, 1H, C(5)H) 6.51 (t, 1H, C(6)H) 7.58 (d, 1H, C(7)H), 7.55 (m, 30H, H (Ph_3)); ^{13}C, δ 171.2 C(1), 118.7 C(2), 128.7 C(3), 154.4 C(4), 111.8 C(5), 110.5 C(6), 140.6 C(7); ^{31}P{^{1}H}, δ 32.0 (s). Single crystals of $[(AuPPh_3)_2(fspa)]$ (**7**) were grown by slow evaporation of a methanolic solution.



Scheme 2

[(AuPPh$_3$)$_2$(tspa)] (8). H$_2$tspa (0.026 g, 1.5 mmol), Au(PPh$_3$)Cl (0.150 g, 3.0 mmol), methanol (12 cm^3), NaOH (0.012 g, 3.0 mmol), H$_2$O (3 cm^3), golden solid. Yield: 74%. Mp 105 °C. Anal. Found: C 46.5, H 3.4, S 5.6. Calc. for $C_{43}H_{34}O_2S_2P_2Au_2$: C 46.0, H 3.2, S 5.7%. MS (FAB): the main metalated signals are at *m*/*z* 1409 (1%), [(AuPPh$_3$)$_3$S]$^+$; 1103 (43), [M]$^+$; 721 (69), [(PPh$_3$)$_2$Au]$^+$; 644 (2), [Au(PPh$_3$)(Htspa)]$^+$; and 459 (100), [(PPh$_3$)Au]$^+$. IR (cm^{-1}): 1571m, ν_{as}(COO); 1478w, 1434m, ν(Ph$_3$P). NMR (DMSO-d$_6$): ^{1}H, δ 8.18 (s, 1H, C(3)H), 7.47 (d, 1H, C(5)H), 7.18 (t, 1H, C(6)H), 7.70 (d, 1H, C(7)H), 7.43 (m, 30H, H (Ph$_3$)); ^{13}C, δ 168.4 C(1), 126.6 C(2), 134.3 C(3), 140.5 C(4), 132.1 C(5), 126.4 C(6), 131.5 C(7); ^{31}P{^{1}H}, δ 32.6 (s). Single crystals of [(AuPPh$_3$)$_2$(tspa)]·2MeOH (**8**·2MeOH) were grown by slow evaporation of a methanolic solution.

[(AuPPh$_3$)$_2$(pspa)]·2MeOH (9·2MeOH). H$_2$pspa (0.045 g, 2.5 mmol), Au(PPh$_3$)Cl (0.250 g, 5.0 mmol), methanol (20 cm^3), NaOH (0.020 g, 5.0 mmol), H$_2$O (5 cm^3), light yellow solid. Yield: 83%. Mp 130 °C. Anal. Found: C 48.3, H 3.7, S 2.6. Calc. for $C_{47}H_{44}O_4SP_2Au_2$: C 48.6, H 3.8, S 2.8%. MS (FAB): the main metalated signals are at *m*/*z* 1409 (6%), [(AuPPh$_3$)$_3$S]$^+$; 1097 (24), [M]$^+$; 721 (68), [(PPh$_3$)$_2$Au]$^+$; and 459 (100), [(PPh$_3$)Au]$^+$. IR and Raman (R) (cm^{-1}): 1581s, 1585s (R), ν_{as}(COO); 1480m, 1436s, ν(Ph$_3$P). NMR (DMSO-d$_6$): ^{1}H, δ 7.50 (s, 1H, C(3)H), 8.00 (d, 2H,C(5)H$_o$), 7.30 (t, 2H, C(6)H$_m$) 7.10 (m, 1H, C(7)H$_p$), 7.55 (m, 30H, H(PPh$_3$)); ^{13}C, δ 170.9 C(1), 127.4 C(2), 141.2 C(3), 138.9 C(4), 130.0 C(5), 125.1 C(6), 128.1 C(7); ^{31}P{^{1}H}, δ 31.6 (s); 30.9 (s) (at low temperature). Single crystals were grown by slow evaporation of a methanolic solution.

Crystallography

X-Ray data collection and reduction. Single crystals of (Htspa)$_2$·Me$_2$CO, [Au(PPh$_3$)(Hfspa)] (**1**), [HQ][Au(PPh$_3$)(pspa)] (**6**), [(AuPPh$_3$)$_2$(fspa)] (**7**), [(AuPPh$_3$)$_2$(tspa)]·2MeOH (**8**·2MeOH) and [(AuPPh$_3$)$_2$(pspa)]·2MeOH (**9**·2MeOH) were mounted on glass fibres for data collection in a Bruker Smart CCD automatic diffractometer at 293 K using Mo-Kα radiation (λ = 0.71073 Å). Table 1 summarizes the crystal data, experimental details and refinement results. Corrections for Lorentz effects, polarization[12] and absorption[13] were made.

The structures were solved by Patterson (**9**) or direct methods [(Htspa)$_2$·Me$_2$CO, **1**, **6**, **7** and **8**·2MeOH].[13] The acetone molecule of (Htspa)$_2$·Me$_2$CO was disordered, as was one of the methanol molecules in both **8**·2MeOH and **9**·2MeOH. For (Htspa)$_2$·Me$_2$CO and **8**·2MeOH we were unable to find a statistical model for the disorder, and the program SQUEEZE[14] was therefore used to correct the reflection data for diffuse scattering. In **9**·2MeOH the disorder was accounted for by a model with the methyl group in two positions with equal occupancy factors (50%). In **8**·2MeOH the phenyl groups were refined as rigid hexagons with C–C distances of 1.39 Å. Otherwise, most non-hydrogen atoms were treated using anisotropic temperature parameters in the last cycle of the refinement; the exceptions being O2M and the disordered methyl carbons of **9**·2MeOH (C2A and C2B), which were refined isotropically. Hydrogen atoms were refined as riders at geometrically calculated[15] positions, except for those of the carboxylate groups in (Htspa)$_2$·Me$_2$CO, **1** and **6**, the NH$_2$ group in **6**, and the alcohol molecules in **8**·2MeOH and **9**·2MeOH, which were located and refined isotropically or fixed (**6**).

CCDC reference numbers 212119–212124.

See http://www.rsc.org/suppdata/dt/b3/b307192h/ for crystallographic data in CIF or other electronic format.

Results and discussion

The 1 : 1 complexes [Au(PPh$_3$)(Hxspa)] (x = f, t, p) were prepared by adding Au(PPh$_3$)Cl to a solution of the appropriate sulfanylcarboxylic acid and KOH in ethanol. Reaction of these 1 : 1 complexes with diisopropylamine afforded compounds [HQ][Au(PPh$_3$)(xspa)]. The 2 : 1 complexes [(AuPPh$_3$)$_2$(xspa)] were prepared by adding a solution of Au(PPh$_3$)Cl in 2 : 1 mole ratio to a solution of the appropriate acid and NaOH in methanol, or by adding Au(PPh$_3$)Cl to a 1 : 1 complex (Scheme 2).

The FAB$^+$ mass spectra of these complexes show the [M]$^+$ peak and other fragments that, as in similar systems,[3] are indicative of the cleavage of the Au–S and Au–P bonds.

(Htspa)$_2$·Me$_2$CO

Single crystals obtained by slow evaporation of an acetone solution of H$_2$tspa were composed of (Htspa)$_2$ dimers formed by oxidation of the acid. (Htspa)$_2$·Me$_2$CO crystallized in the unusual monoclinic space group *P*2/*n*. The asymmetric unit contains two crystallographically independent half-molecules that by rotation around the two-fold axis generate two dimeric molecules (hereinafter denoted molecules A and B) which are associated by hydrogen bonds as shown in Fig. 1. The main bond lengths and angles in A and B are listed in Table 2.

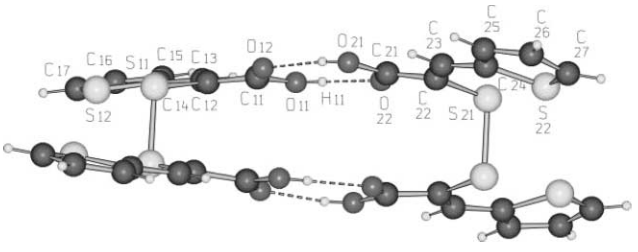


Fig. 1 Crystal structure of (Htspa)$_2$·Me$_2$CO, showing the numbering scheme.

In each molecule, the two Htspa units are linked by a disulfide bridge with an unexceptional S–S distance (2.070(2) and 2.069(2) Å in molecules A and B, respectively; the sum of the covalent radii of two sulfur atoms is 2.04 Å).[16] The Htspa units are essentially planar, with *Z* configuration about the C(12)–C(13) bond and the thiophene sulfur atom *cis* to the sulfanyl sulfur; the angle between their mean planes is 9.7(3)° in A and 16.9(2)° in B.

Molecules A and B are associated by hydrogen bonds between their carboxylic acid groups, and the geometric parameters of these bonds [0.77(4), 1.87(4), 2.630(4) Å, 170(6)° for O(11)–H(11) ··· O(22); 0.82(4), 1.82(4), 2.635(4) Å, 173(5)° for

Table 1 Crystal data for $(Htspa)_2·Me_2CO$, $[Au(PPh_3)(Hfspa)]$ (**1**), $[HQ][Au(PPh_3)(pspa)]$ (**6**), $[(AuPPh_3)_2fspa]$ (**7**), $[(AuPPh_3)_2tspa]·2MeOH$ (**8**·2MeOH) and $[(AuPPh_3)_2pspa]·2MeOH$ (**9**·2MeOH)

Compound	$(Htspa)_2·Me_2CO$	$[Au(PPh_3)(Hfspa)]$ (**1**)	$[HQ][Au(PPh_3)(pspa)]$ (**6**)	$[(AuPPh_3)_2fspa]$ (**7**)	$[(AuPPh_3)_2tspa]·2MeOH$ (**8**·2MeOH)	$[(AuPPh_3)_2pspa]·2MeOH$ (**9**·2MeOH)
Empirical formula	$C_{17}H_{16}O_5S_4$	$C_{25}H_{20}AuO_3PS$	$C_{33}H_{37}AuNO_2PS$	$C_{43}H_{34}Au_2O_3P_2S$	$C_{45}H_{42}Au_2O_4P_2S_2$	$C_{47}H_{44}Au_2O_4P_2S$
M_r	428.54	628.41	739.63	1086.64	1166.78	1160.76
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	7.3669(7)	11.2143(16)	9.8237(12)	9.8209(8)	21.106(3)	21.6565(12)
b/Å	17.7955(17)	27.397(4)	13.9493(17)	17.8496(15)	13.354(2)	13.3177(7)
c/Å	14.8798(15)	15.353(2)	23.244(3)	22.7002(19)	16.268(2)	16.1638(9)
β/°	96.630(2)	91.373(3)	101.027(3)	92.495(2)	111.560(3)	110.8850(10)
U/Å^3	1937.7(3)	4715.6(12)	3126.4(6)	3975.6(6)	4264.4(11)	4356.8(4)
Z	4	8	4	4	4	4
D_c/Mg m^{-3}	1.469	1.770	1.571	1.815	1.817	1.770
μ/mm^{-1}	0.515	6.419	4.853	7.543	7.087	6.890
Crystal size /mm	0.24 × 0.14 × 0.12	0.18 × 0.10 × 0.9	0.22 × 0.14 × 0.08	0.47 × 0.30 × 0.15	0.06 × 0.06 × 0.05	0.25 × 0.22 × 0.10
θ Range for data collection /°	1.79–28.05	1.49–28.02	1.71–28.05	1.45–28.11	1.84–28.05	1.83–28.02
Index ranges	−9 to 9, −23 to 22, −19 to 11	−13 to 14, −33 to 36, −19 to 20	−12 to 12 −18 to 14 −24 to 30	−7 to 12 −23 to 23 −29 to 30	−26 to 27 −17 to 17, −21 to 16	−24 to 28, −10 to 17, −21 to 20
Reflections collected	10907	24394	16614	22785	21094	24708
Unique reflections (R_{int})	4453 (0.0576)	10287 (0.0944)	6895 (0.1080)	9005 (0.0924)	9146 (0.1183)	9848 (0.0945)
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0576, 0.1228	0.0566, 0.0743	0.0471, 0.0580	0.0590, 0.1365	0.0625, 0.1477	0.0457,0.0908
Final $R1$, $wR2$ (all data)	0.1732, 0.1459	0.2698, 0.1083	0.2273, 0.0814	0.1160, 0.1511	0.2542, 0.1821	0.0882, 0.0992

Table 2 Bond lengths (Å) and angles (°) in $(Htspa)_2 \cdot Me_2CO$

Molecule A		Molecule B	
S(11)–C(12)	1.774(4)	S(21)–C(22)	1.767(4)
S(11)–S(11)#1	2.070(2)	S(21)–S(21)#	2.069(2)
S(12)–C(17)	1.711(5)	S(22)–C(27)	1.717(5)
S(12)–C(14)	1.723(4)	S(22)–C(24)	1.717(4)
O(11)–C(11)	1.320(5)	O(21)–C(21)	1.329(4)
O(12)–C(11)	1.214(4)	O(22)–C(21)	1.215(4)
C(11)–C(12)	1.458(5)	C(21)–C(22)	1.456(5)
C(12)–C(13)	1.353(5)	C(22)–C(23)	1.346(5)
C(13)–C(14)	1.422(5)	C(23)–C(24)	1.445(5)
C(12)–S(11)–S(11)#1	103.11(13)	C(22)–S(21)–S(21)#1	102.62(13)
O(12)–C(11)–O(11)	122.4(4)	O(22)–C(21)–O(21)	122.0(4)
O(12)–C(11)–C(12)	123.3(4)	O(22)–C(21)–C(22)	123.6(4)
O(11)–C(11)–C(12)	114.3(4)	O(21)–C(21)–C(22)	114.4(4)
C(13)–C(12)–C(11)	121.0(4)	C(23)–C(22)–C(21)	121.5(4)
C(13)–C(12)–S(11)	122.7(3)	C(23)–C(22)–S(21)	122.2(3)
C(11)–C(12)–S(11)	116.2(3)	C(21)–C(22)–S(21)	116.2(3)
C(12)–C(13)–C(14)	132.2(4)	C(22)–C(23)–C(24)	131.8(4)
C(15)–C(14)–C(13)	122.9(4)	C(25)–C(24)–C(23)	122.5(4)

Symmetry operation: #1 $-x + 3/2, y, -z + 3/2$.

O(21)–H(21) ··· O(12)] are in keeping with the C–O bond lengths in each carboxyl group being in the normal ranges (1.21–1.25 Å for C=O, and 1.31–1.35 Å for C–OH).[17]

[Au(PPh$_3$)(Hxspa)]

The asymmetric unit of the crystal of [Au(PPh$_3$)(Hfspa)] (**1**) contains two molecules with slightly different parameters that are connected by hydrogen bonds between the CO_2H groups and by a weak π-stacking interaction between two PPh_3 phenyl rings. Fig. 2 shows both these molecules, and their most significant structural parameters are listed in Table 3.

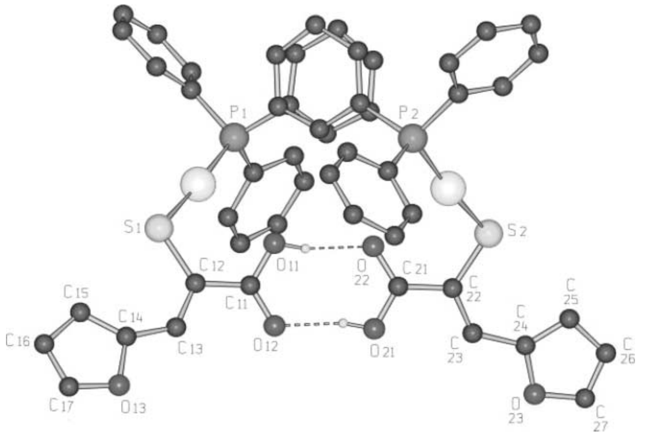


Fig. 2 Interaction by hydrogen bonding and weak π-stacking between the two molecules in the asymmetric unit of [Au(PPh$_3$)(Hfspa)] (**1**) (hydrogen atoms, except those involved in hydrogen bonds, are omitted for clarity).

In both molecules the Au atom is coordinated to S and P atoms in an almost linear arrangement (P(1)–Au(1)–S(1) 176.89(14)°; P(2)–Au(2)–S(2) 174.83°). The Au(1)–O(11) and Au(2)–O(22) distances [3.022(10) and 3.011(10) Å, respectively] are less than the sum of the van der Walls radii of Au and O (3.20 Å)[16] and thus suggest a weak interaction that may be responsible for the slight deviation from linearity of the P–Au–S angle. The Au–S and Au–P bond lengths are close to the values found in other compounds with an S–Au–P fragment.[18]

Although the main parameters of the Hfspa moiety are similar in the two molecules, they differ slightly as regards the planarity of their C(S)–COO fragments, the O(12)–C(11)–C(12)–S(1) and O(22)–C(21)–C(22)–S(2) torsion angles being −166.0° and 16.1°, respectively. The C–S bond lengths are close to those found in $(Htspa)_2 \cdot Me_2CO$ and in complexes of similar ligands,[7,8] and are also close to the theoretical length of a single C–S bond, 1.81 Å.[19] In both molecules the Hfspa moiety exhibits *Z* configuration about the C(12)–C(13) [or C(22)–C(23)] bond, and the O atom of the furan ring is *trans* to the S atom.

Table 3 Selected interatomic distances (Å) and angles (°) in [Au(PPh$_3$)(Hfspa)] (**1**)

(a) Au environment

Au(1)–P(1)	2.255(3)	P(1)–Au(1)–S(1)	176.89(14)
Au(1)–S(1)	2.301(3)	P(1)–Au(1)–O(11)	114.1(2)
Au(1)–O(11)	3.022(10)	S(1)–Au(1)–O(11)	67.9(2)
Au(2)–P(2)	2.258(4)	P(2)–Au(2)–S(2)	174.83
Au(2)–S(2)	2.320(4)	P(2)–Au(2)–O(22)	115.3(2)
Au(2)–O(22)	3.011(10)	S(2)–Au(2)–O(22)	67.8(2)

(b) Hfspa

S(1)–C(12)	1.738(12)	O(12)–C(11)–O(11)	119.5(15)
O(11)–C(11)	1.270(14)	O(12)–C(11)–C(12)	123.3(14)
O(12)–C(11)	1.244(16)	O(11)–C(11)–C(12)	116.8(16)
C(11)–C(12)	1.451(17)	C(13)–C(12)–C(11)	113.7(13)
C(12)–C(13)	1.351(14)	C(13)–C(12)–S(1)	123.0(11)
C(13)–C(14)	1.404(16)	C(11)–C(12)–S(1)	123.0(11)
		C(12)–C(13)–C(14)	128.1(14)
S(2)–C(22)	1.726(13)	O(22)–C(21)–O(21)	118.6(15)
O(21)–C(21)	1.279(14)	O(22)–C(21)–C(22)	123.4(15)
O(22)–C(21)	1.239(14)	O(21)–C(21)–C(22)	118.0(15)
C(21)–C(22)	1.427(17)	C(23)–C(22)–C(21)	116.5(13)
C(22)–C(23)	1.371(16)	C(23)–C(22)–S(2)	123.3(11)
C(23)–C(24)	1.445(19)	C(21)–C(22)–S(2)	120.0(11)
		C(22)–C(23)–C(24)	128.6(15)

The hydrogen bond parameters [0.84, 1.78, 2.603(14) Å, 168° for O(11)–H(11) ··· O(22); 0.83, 1.79, 2.601(15) Å, 166° for O(21)–H(21) ··· O(12)] are in keeping with the C–O bond lengths in each CO_2H group being closer to each other than in $(Htspa)_2 \cdot Me_2CO$.

The existence of a weak π-stacking interaction between the rings [C(231) ··· C(236)] and [C(121) ··· C(126)] is supported by the distance between their centres [3.829(5) Å] and by the shortest interatomic distance between them [C(236) ··· C(125) 3.539(19) Å].

Comparison of the structures of the triphenylphosphinegold(I) sulfanylcarboxylates that have now been characterized by X-ray diffraction {**1**, [Au(PPh$_3$)(SCH$_2$CO$_2$H)],[4] [Au(PPh$_3$)-

(SCH(Me)CO_2H],[2b] [Au(PPh_3)($SCMe_2CO_2H$)],[4] [Au(PPh_3)-(4-$SC_6H_4CO_2H$)],[3] [Au(PPh_3)(2-$SC_6H_4CO_2H$)][5,6] and [Au-(PPh_3)(6-Hmna)][2b]} shows that they have similar Au–S and Au–P bond lengths but exhibit considerable variety as regards their intermolecular interactions, as was emphasized in the Introduction. Compound **1** is the first in which the stability of a dimeric structure created by carboxyl–carboxyl hydrogen bonds appears to be reinforced by π-stacking.

The IR and Raman spectra of [Au(PPh_3)(Hfspa)] do not show the ν(SH) band located at 2568 cm^{-1} in the spectrum of H_2fspa, and the vibrations of the CO_2H group are slightly shifted from their positions in the latter spectrum [1673, ν(C=O); 1417, δ(OH); 1266, ν(C–O)]. Both findings are in keeping with the S-coordination and CO_2H group hydrogen bonding shown by the X-ray study. Similar alterations were found in the spectra of compounds **2**·H_2O and **3**, suggesting that the three 1 : 1 adducts have similar solid state structures.

Since the ligands rapidly decompose in dmso-d_6, ^1H, ^{13}C and ^{31}P NMR data (see Experimental section) were obtained from freshly prepared concentrated solutions. No decomposition of any of the gold complexes was detected under the conditions used. Assignment of the signals was based on HMQC and HMBC experiments and on previous data.[7,8] The broad signal at about 13 ppm in the ^1H NMR spectra of the ligands persists in the complexes, in keeping with the non-deprotonation of the CO_2H group, and the shift of the C(3)H signal to higher field (from 7.60, 8.18 and 7.73 ppm for H_2fspa, H_2tspa and H_2pspa, respectively) is in keeping with the S-coordination found in the solid state.[7,8] This coordination mode is corroborated by the ^{13}C data: the C(3) signal shifts to higher field (from 132.0, 141.2 and 145.6 ppm in H_2fspa, H_2tspa and H_2pspa), and the C(1) signal to lower field (from 166.4, 166.6 and 167.1 in H_2fspa, H_2tspa and H_2pspa). All three complexes have a $^{31}P\{^1H\}$ NMR signal at about 36 ppm, close to those of other triphenylphosphine complexes with S–Au–P fragments.[2b,3]

[HQ][Au(PPh_3)(xspa)]

The X-ray study of [HQ][Au(PPh_3)(pspa)] (**6**) shows the crystal to consist of diisopropylammonium cations and [Au(PPh_3)-(pspa)] anions. Fig. 3 shows an ORTEP plot of the centrosymmetric dimers created by hydrogen bonding between the diisopropylammonium cation and the carboxylate group; significant distances and angles are listed in Table 4. The Au atom is coordinated by the S atom of the dideprotonated pspa ligand and by the triphenylphosphine P atom, and these two bonds are practically collinear. In the Au environment the main difference with respect to **1** is the absence of an Au ··· O interaction, the Au–O distances (3.392(6) and 3.715(5) Å) both being greater than the sum of the van der Waals radii of Au and O (3.20 Å).[16] The absence of this interaction is probably due to the plane of the carboxylate group in the pspa moiety (which adopts *E* configuration about the C(2)–C(3) bond) being almost orthogonal to the S–C(2)–C(1) plane [76.8(3)°] (Fig. 3), whereas in **1** the practically planar C(S)–COOH fragment allows weak Au–O interaction.

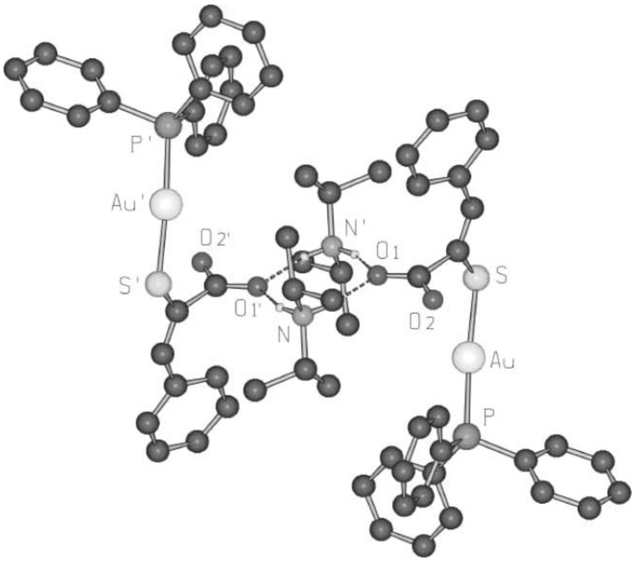


Fig. 3 Crystal structure of [HQ][Au(PPh_3)(pspa)] (**6**), showing the hydrogen bonding between the diisopropylammonium cation and the carboxylate group (symmetry code $' = -x+2, -y+2, z$) Hydrogen atoms, except those involved in hydrogen bonds, are omitted for clarity.

Table 4 Selected interatomic distances (Å) and angles (°) in [HQ][Au(PPh_3)(pspa)] (**6**)

(a) Au environment			
Au–P	2.262(3)	P–Au–S	176.07(10)
Au–S	2.297(3)	P–Au–O(2)	107.94(13)
Au–O(2)	3.392(6)	S–Au–O(2)	73.61(13)
Au–O(1)	3.715(5)	P–Au–O(1)	121.73(13)
		S–Au–O(1)	61.69(12)
(b) pspa			
O(1)–C(1)	1.246(9)	O(1)–C(1)–O(2)	125.4(10)
O(2)–C(1)	1.271(9)	O(1)–C(1)–C(2)	119.7(9)
C(1)–C(2)	1.507(12)	O(2)–C(1)–C(2)	114.8(9)
C(2)–C(3)	1.314(12)	C(3)–C(2)–C(1)	122.3(10)
C(3)–C(4)	1.499(13)	C(1)–C(2)–S	115.3(8)
S–C(2)	1.746(10)	C(2)–C(3)–C(4)	131.3(11)

Hydrogen bonds between the O1 atoms of two anions and the nitrogens of two $[HQ]^+$ cations [N–H(0A) ··· O1 = 0.90, 1.82, 2.699(10) Å, 166° and N–H(0B) ··· O1#1 = 0.90, 1.92, 2.759(9) Å, 154, #1 = $-x + 2, -y + 2, z$] create centrosymmetric dimers. The parameters of the hydrogen bonds and CO groups involved are very similar to those of an arrangement of this kind found by us in [HQ][$SnPh_3$(pspa)].[7] However, in the tin compound the pspa fragment is quasi-planar, enabling a short Sn–O interaction (2.383(2) Å). Both the soft character of the Au atom and steric factors may be responsible for the COO rotation that, as noted above, appears to prevent an analogous interaction in **6**.

Comparison of the IR and Raman spectra of [HQ][Au(PPh_3)-(pspa)] with those of H_2pspa shows the disappearance of the ν(SH) band located at 2567 cm^{-1} in the spectrum of the free acid, and the replacement of the CO_2H bands at 1670 cm^{-1} [ν(C=O)], 1416 cm^{-1} [δ(OH)] and 1266 cm^{-1} [ν(C=O)] by bands typical of a carboxylate group. The slight difference between the positions of these bands and their positions in the IR spectrum of the sodium salt {1574 cm^{-1} [$\nu(CO)_{as}$] and 1383 cm^{-1} [$\nu(CO)_{sym}$]} may be due to the hydrogen bonds present in the complex. A similar pattern was found in this region of the spectra of [HQ][Au(PPh_3)(tspa)] and [HQ][Au(PPh_3)(fspa)], suggesting that all three compounds have the same structure in the solid state.

The ^1H NMR spectra of these compounds show a shift of the C(3)H signal to higher field, which suggests the persistence of the S–Au bond in solution, and the disappearance of the broad signal located at about 13 ppm in the spectrum of the free acid, which shows that the CO_2H group remains deprotonated.

The shift of the C(3) signal in the ^{13}C NMR spectra confirms S-coordination, while the position of the C(1) signal suggests the persistence in solution of the N–H ··· O bond found in the solid state, being closer to positions associated with a monodentate carboxylate group[20] than to its position in the spectra of the corresponding sodium salts in D_2O (175.7, 176.0 and 174.8 ppm for H_2fspa, H_2tspa and H_2pspa, respectively). The positions of the C(1) signal in mixtures of the free acid and diisopropylamine in 1 : 2 mole ratio are 167.2, 168.5 and 170.9 ppm for H_2fspa, H_2tspa and H_2pspa, respectively.

[$(AuPPh_3)_2$(xspa)]

Figs. 4–6 show the structures and numbering schemes of the dinuclear gold complexes [$(AuPPh_3)_2$(fspa)] (**7**), [$(AuPPh_3)_2$-tspa]·2MeOH (**8**·2MeOH) and [$(AuPPh_3)_2$pspa]·2MeOH (**9**·2MeOH), and Table 5 lists their most significant structural parameters.

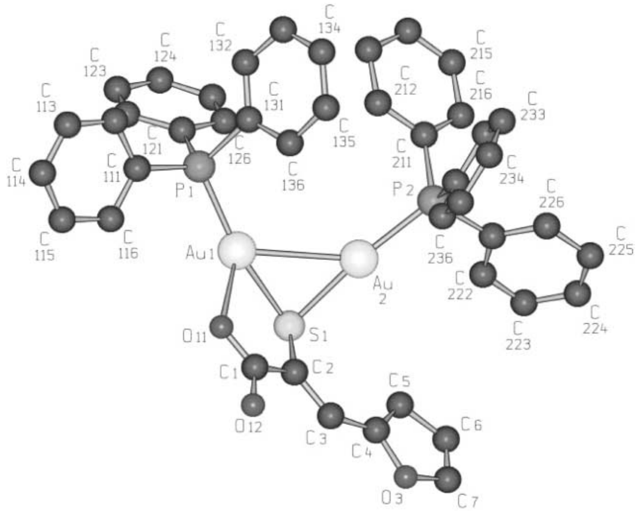


Fig. 4 Structure of [$(AuPPh_3)_2$(fspa)] (**7**) (hydrogen atoms are omitted for clarity).

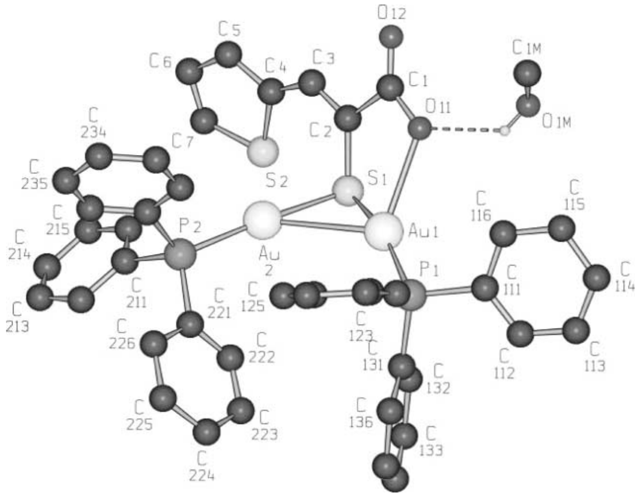


Fig. 5 Structure of [$(AuPPh_3)_2$(tspa)]·2MeOH (**8**·2MeOH) (hydrogen atoms, except those involved in hydrogen bonding, are omitted for clarity).

The crystal of **8**·2MeOH is formed by [$(AuPPh_3)_2$(tspa)] and two methanol molecules, one of which is disordered (see Experimental section). The other one is linked by a hydrogen bond to one of the oxygen atoms of the carboxylate group [O(1M)–H(1M) ··· $O(11)^{\#1}$: 0.82, 2.26, 2.76(2) Å, 119.7°; #1 = x, $y - 1$, z] (Fig. 5). Compound **9** also crystallized with two methanol molecules in the asymmetric unit, but in this case both molecules are hydrogen-bonded to the carboxylate group, the geometric parameters of O(1M)–H(1M) ··· O(11) being 0.92(7), 1.83(8), 2.737(8) Å, 167°; and those of O(2M)–H(2M) ··· O(12) 0.84, 1.88, 2.723(15) Å, 177°] (Fig. 6).

As the figures show, the two gold atoms have different coordination environments. Au(1) is strongly bound not only to the thiolate S atom and to a P atom, but also to a carboxylate O atom, the Au–O(11) distance [2.499(9)–2.637(6) Å] being significantly shorter than both the sum of the van der Waals radii (3.20 Å)[16] and the weak bond in **1**. This interaction probably affects other structural parameters. Thus, whereas the Au(1)–P(1) and Au(2)–P(2) bond lengths are similar and close to the values found in **1** and **6**, Au(1)–S(1) is longer than Au(2)–S(1) and the S–Au–P angle is significantly narrower for Au(1) than for Au(2).

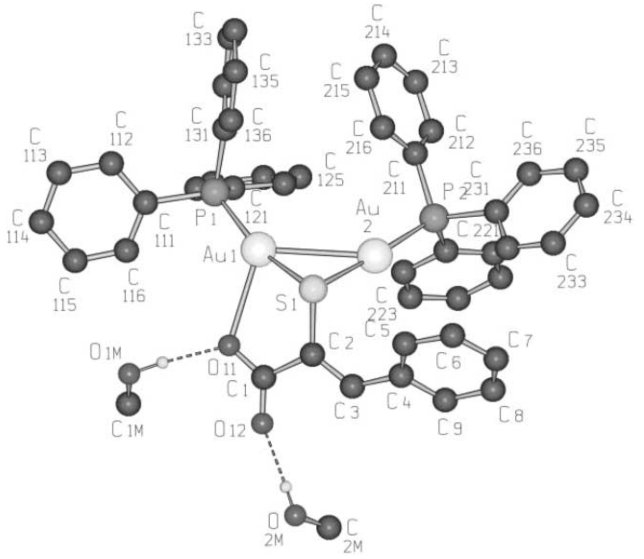


Fig. 6 Structure of [$(AuPPh_3)_2$(pspa)]·2MeOH (**9**·2MeOH) (hydrogen atoms, except those involved in hydrogen bonding, are omitted for clarity).

Table 5 Selected interatomic distances (Å) and angles (°) in the dinuclear complexes **7**, **8**·2MeOH and **9**·2MeOH

(a) Au environment	**7**	**8**·2MeOH	**9**·2MeOH
Au(1)–P(1)	2.248(3)	2.252(4)	2.2484(18)
Au(1)–S(1)	2.361(3)	2.365(5)	2.3534(17)
Au(1)–O(11)	2.499(9)	2.586(15)	2.637(6)
Au(1)–Au(2)	2.9617(6)	3.0325(12)	3.0344(4)
Au(2)–P(2)	2.262(3)	2.265(4)	2.252(2)
Au(2)–S(1)	2.344(3)	2.339(5)	2.329(2)
P(1)–Au(1)–S(1)	164.58(10)	162.112(17)	164.37(7)
P(1)–Au(1)–O(11)	118.7(2)	123.4(4)	122.61(12)
S(1)–Au(1)–O(11)	76.5(2)	73.6(4)	72.06(12)
C(2)–S(1)–Au(1)	103.3(4)	105.6(8)	105.2(2)
Au(2)–S(1)–Au(1)	78.02(8)	80.27(16)	80.78(6)
C(1)–O(11)–Au(1)	117.9(8)	120.5(16)	116.2(5)
P(2)–Au(2)–S(1)	171.34(11)	175.53(19)	175.84(7)
C(2)–S(1)–Au(2)	104.8(3)	102.7(7)	102.8(3)
(b) Ligand			
S(1)–C(2)	1.767(11)	1.73(2)	1.758(8)
O(11)–C(1)	1.255(14)	1.34(2)	1.251(9)
O(12)–C(1)	1.238(14)	1.21(3)	1.225(10)
C(1)–C(2)	1.506(17)	1.61(3)	1.537(10)
C(2)–C(3)	1.362(15)	1.32(2)	1.357(10)
C(3)–C(4)	1.445(16)	1.43(3)	1.471(10)
O(12)–C(1)–O(11)	122.7(13)	131(2)	126.6(8)
O(12)–C(1)–C(2)	119.5(12)	121(2)	118.6(7)
O(11)–C(1)–C(2)	117.5(11)	108(2)	114.8(8)
C(3)–C(2)–C(1)	118.3(10)	113.3(19)	118.3(8)
C(3)–C(2)–S(1)	120.9(9)	124.0(18)	122.7(6)
C(1)–C(2)–S(1)	120.5(8)	122.7(17)	119.0(6)
C(2)–C(3)–C(4)	132.4(11)	131(2)	129.4(8)

In all three compounds the Au(1)–Au(2) distance [2.9617(6)–3.0344(4)] is shorter than the sum of the van der Walls radii for this metal (3.70 Å)[16] and also shorter than the 3.107(1) Å found in the dinuclear derivative of sulfanylbenzoic acid, in which the carboxyl group is protonated and no significant Au–O interaction was found (Au ··· O 3.079 Å),[10] but it is similar to the Au–Au distance in (μ^2-3,4-toluenedithiolato)bis(triphenylphosphino)digold [3.096(2) Å], in which two different environments of gold were observed ($AuPS_2$ and AuPS).[21]

Although as far as we know an environment like that of Au(1) has not previously been reported, its coordination can be compared with those found in gold(I) dithiolates.[21,22] If Au–Au interactions are ignored, these Au atoms have distorted trigonal geometry with AuPSO or $AuPS_2$ kernels. The S–Au–S angles of dithiolates are close to 85°, whereas in **7**–**9**·2MeOH the S–Au–O angles range from 72.10 to 76.5°. In dithiolates the two P–Au–S angles are close to 160 and 115°, whereas in **7**–**9**·2MeOH the P–Au(1)–S and P–Au(1)–O angles lie in the ranges 162–165 and 118–124°, respectively.

In all three structures the sulfanylpropenoate ligand is essentially planar and adopts *Z* configuration about the C(2)–C(3) bond, but whereas the furan O atom is *trans* to the sulfanyl sulfur in **7** the thiophene S atom is *cis* to S(1) in **8**·2MeOH. The two C–O bond lengths in the carboxylate group are different, the longer being C(1)–O(11) due to coordination to Au(1) (and in **8**·2MeOH and **9**·2MeOH to a hydrogen bond with a CH_3OH molecule). Comparison with the other two structures described in this paper shows that the C–S bond length is not very sensitive to whether the S atom is mono- or dimetallated.

In the IR and Raman spectra of the 2 : 1 complexes, the SH bands disappear and the bands due to the CO_2H group in the free ligands are strongly modified due to deprotonation. The asymmetric carboxylate band lies around 1585 cm^{-1}. However, the complexity of the spectra in the 1500–1300 cm^{-1} range prevents sure assignment of $\nu_{sym}(COO^-)$ and consequently prevents calculation of the parameter $\nu_{as}(COO^-) - \nu_{sym}(COO^-)$, which in previous studies[7,8] of complexes of these ligands was used for diagnosis of the coordination mode of the carboxylato group.

In the ^1H NMR spectra of the 2 : 1 complexes the CO_2H signal disappears due to the deprotonation of the ligand. All the other signals are close to those of compounds **1**–**6** in spite of the ligand in **7**–**9**·2MeOH being coordinated to two gold atoms. In all three spectra, the C(3)H signal is shifted to higher field than in that of the free ligand, which as in the cases of **1**–**6** suggests that the S-coordination detected in the solid state is also present in solution.

To investigate whether the Au ··· O interaction detected in the solid state persists in solution, ^{13}C and ^{31}P spectra were recorded. The ^{13}C spectra show C(1) signals shifted to higher field than in the spectra of the sodium salts, to positions associated with a monodentate carboxylic acid[7,20] (specifically, to 171.2, 168.4 and 170.9 ppm in dmso-d_6 and 170.7, 170.4 and 171.9 ppm in chloroform), suggesting that in both solvents the Au ··· O interaction does persist. Although the solid-state structures of these dinuclear complexes contain two different Au–PPh_3 fragments and the ^{13}C data suggest that the same holds in solution, the ^{31}P NMR spectrum in chloroform consists of just a single resonance even at low temperature (−60 °C), probably due to fluxional behaviour of the two Au–PPh_3 units in solution.[22]

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