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Synthesis and antimicrobial activities of gold(I) sulfanylcarboxylates

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Abstract Reaction of $NaAuCl_4 \cdot H_2O$ and thiodiglycol (1:3 molar ratio) with 3-(aryl)-2-sulfanylpropenoic acids, H_2xspa=[*x:p*=3-phenyl-, *f*=3-(2-furyl)-, *t*=3-(2-thienyl)-, *o-py*=3-(2-pyridyl)-, *Clp*=3-(2-chlorophenyl)-, *-o-mp*=3-(2-methoxyphenyl)-, *-p-mp*=3-(4-methoxyphenyl)-, *-o-hp*=3-(2-hydroxyphenyl)-, *-p-hp*=3-(4-hydroxyphenyl)-, *diBr-o-hp*=3-(3,5-dibromo-2-hydroxyphenyl)] and 2-cyclopentylidene-2-sulfanylacetic acid (H_2cpa) in a 1:1 metal/ligand molar ratio gave compounds of the type [Au(H*x*spa)] or [Au(Hcpa)]. These compounds were reacted with diisopropylamine to afford [HQ][Au(*x*spa)] or [HQ][Au(cpa)] (HQ=diisopropylammonium) and with NaOH to afford $Na[Au(xspa)] \cdot H_2O$ and $Na[Au(cpa)] \cdot H_2O$. All of the new compounds were isolated and characterised by IR and ^1H and ^{13}C NMR spectroscopy. The antimicrobial activities of the complexes against *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, *Candida albicans*, *Pseudomonas aeruginosa* and carbapenem-resistant *P. aeruginosa* were evaluated and compared to those of the equivalent silver(I) complexes. The comparison shows that the gold compounds generally show better activity than the silver analogues against *S. aureus* and *B. subtilis*, but low sensitivity against *E. coli, P. aeruginosa* and *C. albicans*, suggesting a different mode of antimicrobial action for equivalent silver and gold compounds.

Keywords Gold(I) complexes · Sulfanylpropenoic acids · 2-Cyclopentylidene-2-sulfanylacetic acid · Antimicrobial studies

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Introduction

Silver(I) and gold(I) compounds present a variety of biological activities and have various medicinal uses, the study of which has increased in recent years. Silver compounds have mainly been studied for their widely known antibacterial effect; in fact, silver nitrate and certain silver complexes are still used against local infections [1–3]. From this perspective, compounds with Ag kernels have recently been prepared and studied, including examples containing Ag–N [4–7], Ag–O [8–10] and Ag–S [11–15] bonds and some with other additional bonds. In previous papers, we have contributed [14, 15] to the study of Ag–S by preparing compounds of the type [Ag(HL)], $[Ag_2(L)]$, [HQ][Ag(L)] (HQ=diisopropylammonium) and $Na[Ag(L)] \cdot xH_2O$, where H_2L is a 3-(aryl)-2-sulfanylpropenoic acid or 2-cyclopentylidene-2-sulfanylacetic acid, which can be present as a mono- or bideprotonated system in the complexes. The last two classes of compounds, especially the latter, show activity against certain Gram-positive and Gram-negative bacteria, and also against the yeast *Candida albicans*; this activity is similar to that shown by other compounds with Ag–N and/or Ag–O bonds except in the case of *Escherichia coli*, for which they show only low activity.

Studies on gold complexes have mainly focused on anti-arthritic properties [16–21], but growing interest is evident in antitumoral [22–24], antiparasitic [25] and antibacterial

activities. In this last field, the compounds under investigation include a major collection of the type R_3PAuL, in which the gold atom is coordinated to a phosphine ligand and L is an O- [26, 27], N- [28, 29], Cl- [30] or S-[29, 31–35] donor ligand. Complexes including S-donor ligands as the only ligand include the anionic complexes $H[Au(Hmna)_2]$, $Na_3[Au(mna)_2]$ (H_2mna=2-mercaptonicotinic acid) [13] and the cationic complexes $[Au(L)_2](NO_3)_3$ (L=1-[2-(acridin-9-ylamino)ethyl]-1,3-dimethylthiourea) [34]. For the latter ligand, compounds of the type [Au(L)]Br, [Au(L)]SCN and [Au(L)]Cl were also prepared [34] and the coexistence of an S-donor ligand and a Cl ligand was also described for [LAuCl] (where L=2,3-diphenyl-1,3,4-thiadiazolium-5-thiolato-S_{exo}) [36].

The activity of some of these complexes is significant against some bacteria or mycobacteria; however, there is a limited number of gold(I) complexes of this class that have been studied and a broad comparative study with equivalent silver(I) complexes having similar ligand/metal stoichiometry has not been carried out.

As mentioned above, we have previously prepared [14, 15] several silver(I) complexes containing a variety of sulfanylcarboxylate ligands, thus enabling the aforementioned comparative study. In order to carry out this comparison, we have prepared and characterised equivalent gold(I) complexes of the type [Au(HL)], [HQ][Au(L)] (HQ=diisopropylammonium) and $Na[Au(L)]\cdot H_2O$. The activities of these complexes were determined and analysed in light of the results obtained for the equivalent silver(I) complexes.

Experimental

Materials and methods

The 3-(aryl)-2-sulfanylpropenoic acids (Scheme 1) were prepared by condensation of the appropriate aldehyde with rhodanine, subsequent hydrolysis in an alkaline medium and acidification with aqueous HCl. In the preparation of 2-cyclopentylidene-2-sulfanylacetic acid, a ketone (cyclopentanone) was used in the condensation reaction instead of an aldehyde [14, 15, 37]. $NaAuCl_4\cdot 2H_2O$ (Aldrich), S$(CH_2CH_2OH)_2$ (Aldrich), diisopropylamine (Merck) and NaOH (Probus) were all used as supplied.

Elemental analyses were performed on a Fisons 1108 microanalyser. Melting points were determined with a Büchi apparatus. IR spectra (KBr pellets or Nujol mulls) were recorded on a Bruker IFS66V FT-IR spectrophotometer and are reported in the synthesis section using the following abbreviations: vs=very strong, s=strong, m=medium, w=weak, sh=shoulder, br=broad. ^{1}H, ^{13}C and DEPT NMR spectra in solution were recorded in dimethyl sulfoxide (DMSO)-d_6 at room temperature on a Bruker AMX 300 spectrometer operating at 300.14 MHz (^{1}H) and 75.40 MHz (^{13}C), using 5-mm o.d. tubes; chemical shifts are reported relative to TMS using the solvent signal (δ ^{1}H=2.50 ppm; δ ^{13}C=39.50 ppm) as reference. The splitting of proton resonances in the reported ^{1}H NMR spectra are defined as s=singlet, d=doublet, t=triplet, m=multiplet, pst=pseudotriplet and br=broad. The numbering scheme is shown in Scheme 1.

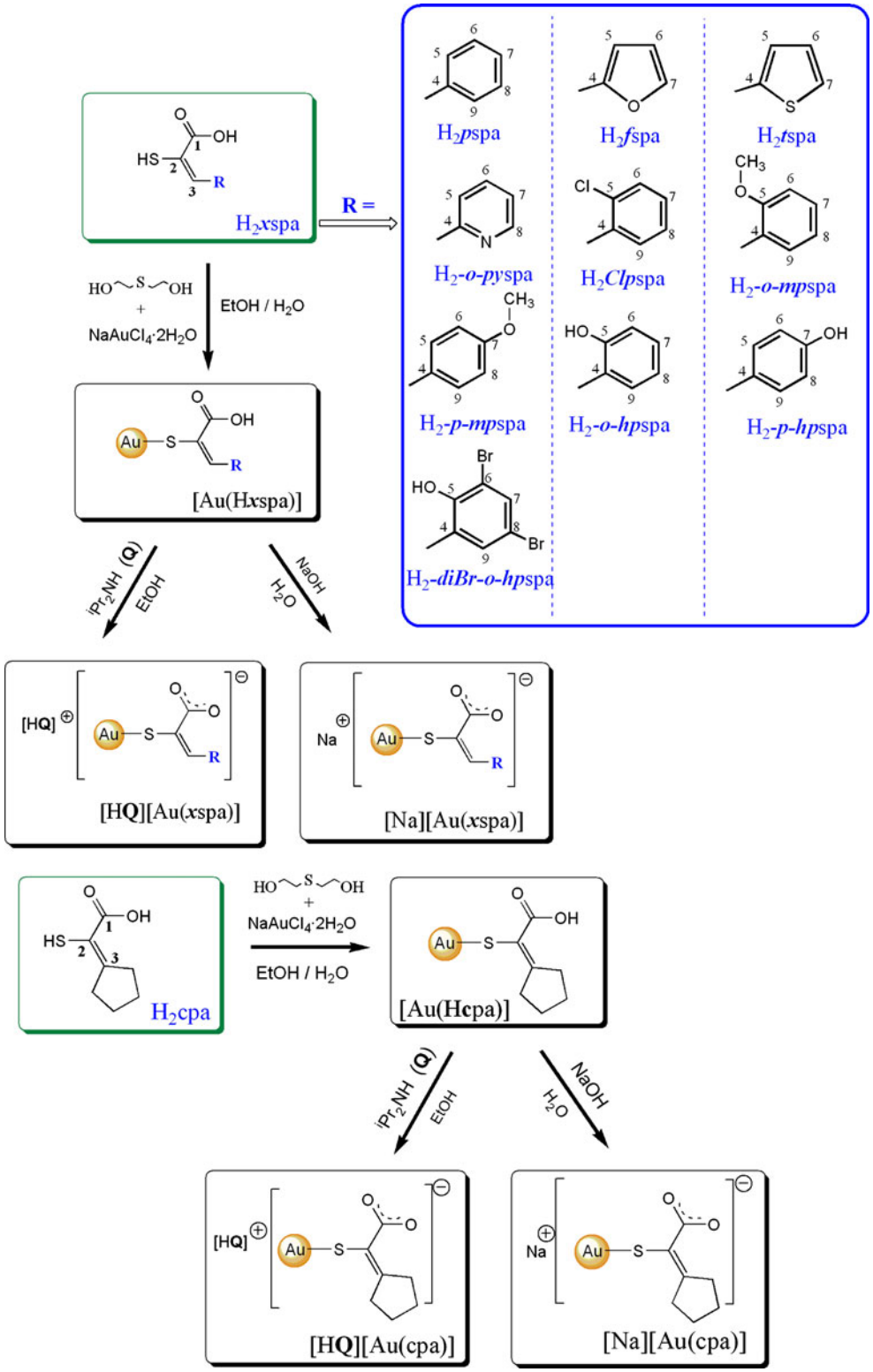
Antimicrobial activity

Antibacterial activity was initially assayed by Müller–Hinton agar diffusion methods. Compounds 1–11 were suspended in water containing 0.1% of DMSO, the ligands and compounds 12–22 were dissolved in ethanol and compounds 23–33 were dissolved in water. Paper discs (5 mm in diameter) were impregnated with 20 μL of a 2 mg/cm^3 solution or suspension of the substance to be tested and control discs were impregnated with solvent alone. The discs were then placed on dishes of Müller–Hinton agar inoculated with *Staphylococcus aureus* (ATCC29213), *Bacillus subtilis* (ATCC6633), *Escherichia coli* (ATCC25922), *Pseudomonas aeruginosa* (ATCC27853) and a carbapenem-resistant strain of *P. aeruginosa* (hereafter "resistant *P. aeruginosa*"). After incubation for 24 h at 37°C, the diameters of the bacterial growth inhibition zones were measured. All assays were carried out in duplicate. For products that showed activity, serial dilutions in Müller–Hinton broth were used as described in the literature [38] to determine the minimum inhibitory concentration (MIC), which is defined as the lowest concentration of the substance under test that inhibits the visible growth of the test organism when the latter is at optimal concentration. Minimum bactericidal concentration (MCB) was also determined for active compounds. Briefly, after MIC determination (24 h of exposure to compounds) bacterial cultures were subcultured in plates of solid medium without test compounds and incubated for 24 h. MCB was defined as the lowest concentration able to prevent bacterial growth in the first 24 h after compound removal.

Synthesis

Complexes of the type [Au(HL)] Complexes **1**–**11** were prepared by adding a stirred solution of $NaAuCl_4\cdot H_2O$ and S$(CH_2CH_2OH)_2$ (thiodiglycol) in a 1:3 molar ratio in water to a solution of the appropriate sulfanylcarboxylic acid (metal/ligand molar ratio 1:1) in ethanol. The mixture was stirred at room temperature for 1 h and the resulting solid was filtered off, washed with ethanol, water and ether and dried in vacuo.

[Au(Hpspa)] (**1**). H_2pspa (0.07 g, 0.38 mmol), $NaAuCl_4\cdot 3H_2O$ (0.15 g, 0.38 mmol), thiodiglycol (0.11 cm^3), ethanol (3 cm^3), H_2O (5 cm^3), yellow solid.



Scheme 1 The numbering scheme of 3-(aryl)-2-sulfanylpropenoic acids and 2-cyclopentylidene-2-sulfanylacetic acid and synthesis of complexes

Yield: 75%; mp: 190°C. (Found: C 28.5, H 1.7, S 8.7%. Calc. for $C_9H_7O_2SAu$: C 28.7, H 1.9, S 8.5%). IR (cm^{-1}): 1,680 vs, ν(C=O); 1,446 s, δ(OH); 1,253 vs, ν(C–O). NMR (DMSO-d_6): ^{1}H, δ 13.14 (s, 1H, C(1) OH), 7.84 (s, 1H, C(3)H), 7.67 (d, 2H, C(5)H, C(9)H), 7.41 (pst, 2H, C(6)H, C(8)H), 7.28 (m, 1H, C(7)H); ^{13}C, δ 166.0 C(1), 128.8 C(2), 144.3 C(3), 133.7 C(4), 130.6 C(5) and C(9), 128.3 C(6) and C(8), 129.9 C(7).

[Au(Hfspa)] (**2**). H_2fspa (0.06 g, 0.38 mmol), $NaAuCl_4 \cdot 3H_2O$ (0.15 g, 0.38 mmol), thiodiglycol

(0.11 cm^3), ethanol (3 cm^3), H_2O (5 cm^3), brown solid. Yield: 86%; mp: 182°C. (Found: C 22.8, H 1.4, S 8.5%. Calc. for $C_7H_5O_3SAu$: C 23.0, H 1.4, S 8.8%). IR (cm^{-1}): 1,663 vs, ν(C=O); 1,466 vs, δ(OH); 1,281 vs br, ν(C–O). NMR (DMSO-d_6): ^1H, δ 12.97 (brs, 1H, C (1)OH), 7.61 (s, 1H, C(3)H), 7.25 (d, 1H, C(5)H), 6.68 (m, 1H, C(6)H), 7.89 (d, 1H, C(7)H); ^{13}C, δ 165.9 C(1), 124.0 C(2), 131.5 C(3), 149.4 C(4), 118.4 C(5), 113.0 C(6), 146.3 C(7).

[Au(Htspa)] (**3**). H_2tspa (0.07 g, 0.38 mmol), $NaAuCl_4{\cdot}3H_2O$ (0.15 g, 0.38 mmol), thiodiglycol (0.11 cm^3), ethanol (3 cm^3), H_2O (5 cm^3), green solid. Yield: 85%; mp: 207°C. (Found: C 22.3, H 1.2, S 16.5%. Calc. for $C_7H_5O_2S_2Au$: C 22.0, H 1.3, S 16.8%). IR (cm^{-1}): 1,674 vs, ν(C=O); 1,408 s, δ(OH); 1,270 vs, ν(C–O). NMR (DMSO-d_6): ^1H, δ 12.57 (brs, 1H, C(1)OH), 8.19 (s, 1H, C(3)H), 7.67 (d, 1H, C(5)H), 7.17 (pst, 1H, C(6)H), 7.89 (d, 1H, C(7)H); ^{13}C, δ 166.1 C(1), 123.0 C(2), 137.6 C(3), 137.6 C(4), 140.3 C(5), 127.1 C(6), 134.2 C(7).

[Au(H-*o*-pyspa)] (**4**). H_2-*o*-pyspa (0.07 g, 0.38 mmol), $NaAuCl_4{\cdot}3H_2O$ (0.15 g, 0.38 mmol), thiodiglycol (0.11 cm^3), ethanol (3 cm^3), H_2O (5 cm^3), pale yellow solid. Yield: 85%; mp: 190°C. (Found: C 25.4, H 1.5, N 3.4, S 8.3%. Calc. for $C_8H_6O_2SNAu$: C 25.5, H 1.6, N 3.7, S 8.5%). IR (cm^{-1}): 1,694 s, ν(C=O); 1,466 m br, δ(OH); 1,250 vs, ν(C–O). NMR (DMSO-d_6): ^1H, δ 7.00 (s, 1H, C(3)H), 8.30 (d, 1H, C(5)H), 8.10 (pst t, 1H, C(6) H), 7.22 (pst, 1H, C(7)H), 8.55 (d, 1H, C(8)H); ^{13}C, δ 165.1 C(1), 136.0 C(2), 134.1 C(3), 154.5 C(4), 150.0 C (5), 134.0 C(6), 121.0 C(7), 124.0 C(8).

[Au(HClpspa)] (**5**). H_2Clpspa (0.08 g, 0.38 mmol), $NaAuCl_4{\cdot}3H_2O$ (0.15 g, 0.38 mmol), thiodiglycol (0.11 cm^3), ethanol (3 cm^3), H_2O (5 cm^3), yellow solid. Yield: 84%; mp: 183°C. (Found: C 26.6, H 1.3, S 7.5%. Calc. for $C_9H_6O_2SClAu$: C 26.3, H 1.5, S 7.8%). IR (cm^{-1}): 1,689 vs, ν(C=O); 1,436 s, δ(OH); 1,247 s, ν(C–O). NMR (DMSO-d_6): ^1H, δ 13.53 (brs, 1H, C (1)OH), 7.86 (s, 1H, C(3)H), 7.46 (d, 1H, C(6)H), 7.31 (pst t, 2H, C(7)H), 7.38 (pst, 2H, C(8)H), 7.61 (d, 1H, C (9)H); ^{13}C, δ 166.6 C(1), 127.8 C(2), 139.7 C(3), 132.5 C(4), 133.5 C(5), 130.7 C(6), 131.3 C(7), 126.9 C(8), 129.3 C(9).

[Au(H-*o*-mpspa)] (**6**). H_2-*o*-mpspa (0.08 g, 0.38 mmol), $NaAuCl_4{\cdot}3H_2O$ (0.15 g, 0.38 mmol), thiodiglycol (0.11 cm^3), ethanol (3 cm^3), H_2O (5 cm^3), pale yellow solid. Yield: 77%; mp: 203°C. (Found: C 29.2, H 2.5, S 8.0%. Calc. for $C_{10}H_9O_3SAu$: C 29.6, H 2.2, S 7.9%). IR (cm^{-1}): 1,685 vs, ν(C=O); 1,463 s, δ(OH); 1,249 vs, ν(C–O). NMR (DMSO-d_6): ^1H, δ 13.15 (brs, 1H, C(1) OH), 8.00 (s, 1H, C(3)H), 7.70 (d, 1H, C(6)H), 6.97 (pst, 1H, C(7)H), 7.40 (t, 1H, C(8)H), 7.05 (d, 1H, C(9) H), 3.79 (s, 3H, OCH_3); ^{13}C, δ 167.1 C(1), 128.8 C(2), 139.4 C(3), 122.3 C(4), 157.5 C(5), 111.1 C(6), 131.6 C(7), 119.8 C(8), 130.3 C(9), 55.5 C(OCH_3).

[Au(H-*p*-mpspa)] (**7**). H_2-*p*-mpspa (0.08 g, 0.38 mmol), $NaAuCl_4{\cdot}3H_2O$ (0.15 g, 0.38 mmol), thiodiglycol (0.11 cm^3), ethanol (3 cm^3), H_2O (5 cm^3), yellow solid. Yield: 92%; mp: 215°C. (Found: C 29.5, H 2.2, S 7.5%. Calc. for $C_{10}H_9O_3SAu$: C 29.6, H 2.2, S 7.9%). IR (cm^{-1}): 1,674 vs, ν (C=O); 1,438 m, δ(OH); 1,256 vs br, ν(C–O). NMR (DMSO-d_6): ^1H, δ 13.10 (brs, 1H, C (1)OH), 7.79 (s, 1H, C(3)H), 7.83 (d, 2H, C(5)H, C(9) H), 6.95 (d, 2H, C(6)H, C(8)H), 3.80 (s, 3H, OCH_3); ^{13}C, δ 166.5 C(1), 125.1 C(2), 144.8 C(3), 126.2 C(4), 133.0 C(5) and C(9), 113.8 C(6) and C(8), 160.7 C(7), 55.3 C(OCH_3).

[Au(H-*o*-hpspa)] (**8**). H_2-*o*-hpspa (0.07 g, 0.38 mmol), $AuCl_4Na{\cdot}3H_2O$ (0.15 g, 0.38 mmol), thiodiglycol (0.11 cm^3), ethanol (3 cm^3), H_2O (5 cm^3), orange solid. Yield: 91%; mp: 190°C. (Found: C 27.6, H 1.8, S 8.6%. Calc. for $C_9H_7O_3SAu$: C 27.6, H 1.8, S 8.2%). IR (cm^{-1}) 1,686 vs, ν(C=O); 1,452 s, δ(OH); 1,250 vs, ν(C–O). NMR (DMSO-d_6): ^1H, δ 13.16 (brs, 1H, C(1)OH), 7.97 (s, 1H, C(3)H), 9.99 (s, 1H, C(5)OH), 7.84 (d, 1H, C(6)H), 7.10 (pst, 1H, C(7)H), 6.82 (pst, 1H, C(8)H), 7.75 (d, 1H, C(9)H); ^{13}C, δ 167.5 C(1), 121.4 C(2), 139.0 C(3), 123.2 C(4), 156.0 C(5), 115.4 C(6), 131.1 C(7), 118.2 C(8), 130.9 C(9).

[Au(H-*p*-hpspa)] (**9**). H_2-*p*-hpspa (0.07 g, 0.38 mmol), $NaAuCl_4{\cdot}3H_2O$ (0.15 g, 0.38 mmol), thiodiglycol (0.11 cm^3), ethanol (3 cm^3), H_2O (5 cm^3), orange solid. Yield: 65%; mp: 205°C. (Found: C 27.5, H 2.0, S 8.2%. Calc. for $C_9H_7O_3SAu$: C 27.6, H 1.8, S 8.2%). IR (cm^{-1}): 1,675 vs, ν(C=O); 1,433 m, δ(OH); 1,245 s br, ν(C–O). NMR (DMSO-d_6): ^1H, δ 12.91 (brs, 1H, C (1)OH), 7.74 (s, 1H, C(3)H), 7.77 (d, 2H, C(5)H, C(9) H), 6.77 (d, 2H, C(6)H, C(8)H), 10.18 (s, 1H, C(7)OH); ^{13}C, δ 166.7 C(1), 123.6 C(2), 145.4 C(3), 124.7 C(4), 133.4 C(5) and C(9), 115.3 C(6) and C(8), 159.7 C(7).

[Au(H-diBr-*o*-hpspa)] (**10**). H_2diBr-*o*-hpspa (0.13 g, 0.38 mmol), $NaAuCl_4{\cdot}3H_2O$ (0.15 g, 0.38 mmol), thiodiglycol (0.11 cm^3), ethanol (3 cm^3), H_2O (5 cm^3), yellow solid. Yield: 83%; mp: 238°C. (Found: C 19.8, H 0.8, S 5.5%. Calc. for $C_9H_5O_3SBr_2Au$: C 19.6, H 0.9, S 5.8%). IR (cm^{-1}): 1,690 vs, ν(C=O); 1,448 vs, δ(OH); 1,255 vs, ν(C–O). NMR (DMSO-d_6): ^1H, δ 13.30 (brs, 1H, C(1)OH), 7.87 (s, 1H, C(3)H), 9.95 (brs, 1H, C(5)OH), 7.75 (s, 1H, C(7)H), 7.59 (s, 1H, C(9)H); ^{13}C, δ 166.7 C(1), 126.5 C(2), 132.1 C(3), 127.0 C(4), 151.3 C(5), 112.8 C(6), 137.4 C(7), 110.6 C(8), 135.1 C(9).

[Au(Hcpa)] (**11**). H_2cpa (0.06 g, 0.38 mmol), $NaAuCl_4{\cdot}3H_2O$ (0.15 g, 0.38 mmol), thiodiglycol (0.11 cm^3), ethanol (3 cm^3), H_2O (5 cm^3), brown solid.

Yield: 80%; mp: 207°C. (Found: C 23.5, H 2.6, S 9.3%. Calc. for $C_7H_9O_2SAu$: C 23.7, H 2.6, S 9.0%). IR (cm^{-1}): 1,668 vs, ν(C=O); 1,413 vs, δ(OH); 1,274 vs, ν(C–O). NMR (DMSO-d_6): ^1H, δ 12.52 (brs, 1H, C(1)OH), 2.67 (m, 2H, C(4)H_2), 1.67 (m, 2H, C(5)H_2), 1.57 (m, 2H, C(6)H_2), 2.56 (m, 2H, C(7)H_2); ^{13}C, δ 171.3 C(1), 119.7 C(2), 166.5 C(3), 36.0 C(4), 26.5 C(5), 25.0 C(6), 35.0 C(7).

Complexes of the type [HQ][Au(L)] Complexes **12**–**22** (HQ=diisopropylammonium) were prepared by adding diisopropylamine to a suspension of the appropriate [Au(HL)] complex in ethanol. The mixture was stirred at room temperature for 24 h. The resulting solid was filtered off and dried in vacuo, and the ethanol was evaporated from the filtrate at room temperature.

[HQ][Au(pspa)] (**12**). [Au(Hpspa)] (0.08 g, 0.20 mmol), diisopropylamine (0.03 cm^3 0.20 mmol), ethanol (9 cm^3), white solid. Yield: 75%; mp: 207°C. (Found: C 37.5, H 4.2, S 6.5, N 2.8%. Calc. for $C_{15}H_{22}O_2SNAu$: C 37.7, H 4.6, S 6.7, N 2.9%). IR (cm^{-1}): 1,629 s, ν(NH_2^+); 1,569 s, $\nu_{asym}(CO_2^-)$; 1,345 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.60 (s, 1H, C(3)H), 7.42 (d, 2H, C(5)H, C(9)H), 7.33 (pst, 2H, C(6)H, C(8)H), 7.20 (m, 1H, C(7)H), 1.19 (d, 12H, [Q]CH_3), 3.23 (m, 2H, [Q]CH); ^{13}C, δ 171.9 C(1), 127.4 C(2), 143.0 C(3), 136.8 C(4), 130.3 C(5) and C(9), 128.2 C(6) and C(8), 129.6 C(7), 46.1 CH[HQ], 19.6 CH_3[HQ].

[HQ][Au(fspa)] (**13**). [Au(Hfspa)] (0.07 g, 0.20 mmol), diisopropylamine (0.03 cm^3 0.20 mmol), ethanol (8 cm^3), brown solid. Yield: 63%; mp: 194°C. (Found: C 33.2, H 4.3, S 6.9, N 2.8%. Calc. for $C_{13}H_{20}O_3SNAu$: C 33.4, H 4.3, S 6.9, N 3.0%). IR (cm^{-1}): 1,621 s br, ν(NH_2^+); 1,553 s br, $\nu_{asym}(CO_2^-)$; 1,339 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.40 (s, 1H, C(3)H), 7.13 (d, 1H, C(5)H), 6.55 (m, 1H, C(6)H), 7.66 (d, 1H, C(7)H), 1.24 (d, 12H, [Q]CH_3), 3.29 (m, 2H, [Q]CH), 8.97 (s, 2H, [Q]NH_2^+); ^{13}C, δ 170.2 C(1), 34.8 C(2), 122.8 C(3), 152.6 C(4), 111.8 C(5), 110.5 C(6), 141.8 C(7), 5.3 CH[HQ], 19.3 CH_3[HQ].

[HQ][Au(tspa)] (**14**). [Au(Htspa)] (0.07 g, 0.16 mmol), diisopropylamine (0.024 cm^3 0.16 mmol), ethanol (8 cm^3), brown solid. Yield: 53%; mp: 203°C. (Found: C 32.0, H 4.3, S 13.4, N 2.6%. Calc. for $C_{13}H_{24}O_2S_2$-NAu: C 32.3, H 4.2, S 13.3, N 2.9%). IR (cm^{-1}): 1,622 vs, ν(NH_2^+); 1,565 vs, $\nu_{asym}(CO_2^-)$; 1,334 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.77 (s, 1H, C(3)H), 7.31 (d, 1H, C(5)H), 7.04 (pst, 1H, C(6)H), 7.54 (d, 1H, C(7)H), 1.24 (d, 12H, [Q]CH_3), 3.27 (m, 2H, [Q]CH), 9.07 (s, 2H, [Q]NH_2^+); ^{13}C, δ 169.9 C(1), 24.9 C(2), 36.1 C(3), 41.9 C(4), 132.5 C(5), 126.7 C(6), 126.2 C(7), 5.6 CH[HQ], 18.9 CH_3[HQ].

[HQ][Au(-*o*-pyspa)] (**15**). [Au(H-*o*-pyspa)] (0.06 g, 0.17 mmol), diisopropylamine (0.026 cm^3, 0.17 mmol), ethanol (7 cm^3), orange solid. Yield: 76%; mp: 194°C. (Found: C 34.9, H 4.6, S 6.5, N 5.6%. Calc. for $C_{14}H_{21}O_2SN_2Au$: C 35.1, H 4.4, S 6.7, N 5.9%). IR (cm^{-1}): 1,610 m sh, ν(NH_2^+); 1,579 vs, $\nu_{asym}(CO_2^-)$; 1,354 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 6.99 (s, 1H, C(3)H), 7.63 (d, 1H, C(5)H), 7.82 (pst, 1H, C(6)H), 7.20 (pst, 1H, C(7)H), 8.32 (d, 1H, C(8)H), 3.18 (d, 12H, [Q]CH_3), 1.19 (m, 2H, [Q]CH); ^{13}C, δ 170.3 C(1), 134.8 C(2), 137.2 C(3), 152.0 C(4), 143.5 C(5), 130.3 C(6), 122.3 C(7), 126.8 C(8), 45.9 CH[HQ], 18.8 CH_3[HQ].

[HQ][Au(Clpspa)] (**16**). [Au(HClpspa)] (0.05 g, 0.16 mmol), diisopropylamine (0.024 cm^3 0.16 mmol), ethanol (6 cm^3), white solid. Yield: 88%; mp: 179°C. (Found: C 34.9, H 4.2, S 6.4, N 2.8%. Calc. for $C_{15}H_{21}O_2SNClAu$: C 35.2, H 4.1, S 6.3, N 2.7%). IR (cm^{-1}): 1,623 vs, ν(NH_2^+); 1,570 vs br, $\nu_{asym}(CO_2^-)$; 1,346 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.66 (s, 1H, C(3)H), 7.40 (d, 1H, C(6)H), 7.13 (m, 1H, C(7)H, C(8)H), 7.47 (d, 1H, C(9)H), 1.21 (d, 12H, [Q]CH_3), 3.29 (m, 2H, [Q]CH), 9.10 (s, 2H, [Q]NH_2^+); ^{13}C, δ 171.8 C(1), 125.8 C(2), 136.5 C(3), 135.1 C(4), 134.3 C(5), 130.2 C(6), 131.0 C(7), 136.6 C(8), 128.9 C(9), 45.8 CH[HQ], 19.2 CH_3[HQ].

[HQ][Au(-*o*-mpspa)] (**17**). [Au(H-*o*-mpspa)] (0.07 g, 0.17 mmol), diisopropylamine (0.027 cm^3, 0.17 mmol), ethanol (8 cm^3), beige solid. Yield: 66%; mp: 177°C. (Found: C 37.4, H 4.5, S 6.8, N 2.5%. Calc. for $C_{16}H_{24}O_3SNAu$: C 37.9, H 4.8, S 6.3, N 2.8%). IR (cm^{-1}): 1,620 vs, ν(NH_2^+); 1,565 vs, $\nu_{asym}(CO_2^-)$; 1,346 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.53 (s, 1H, C(3)H), 7.67 (d, 1H, C(6)H), 6.90 (m, 2H, C(7)H and C(9)H), 7.15 (pst, 1H, C(8)H), 3.75 (s, 3H, OCH_3), 1.21 (d, 12H, [Q]CH_3), 3.24 (m, 2H, [Q]CH), 8.80 (s, 2H, [Q]NH_2^+); ^{13}C, δ 168.7 C(1), 129.0 C(2), 137.3 C(3), 125.0 C(4), 156.8 C(5), 110.5 C(6), 133.4 C(7), 119.3 C(8), 130.6 C(9), 55.1 C(OCH_3), 45.5 CH[HQ], 19.0 CH_3[HQ].

[HQ][Au(-*p*-mpspa)] (**18**). [Au(H-*p*-mpspa)] (0.07 g, 0.17 mmol), diisopropylamine (0.027 cm^3, 0.17 mmol), ethanol (8 cm^3), pale orange solid. Yield: 67%; mp: 198°C. (Found: C 37.9, H 4.6, S 6.2, N 2.6%. Calc. for $C_{16}H_{24}O_3SNAu$: C 37.9, H 4.8, S 6.3, N 2.8%). IR (cm^{-1}): 1,627 m, ν(NH_2^+); 1,570 vs, $\nu_{asym}(CO_2^-)$; 1,348 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.41 (s, 1H, C(3)H), 7.66 (d, 2H, C(5)H, C(9)H), 6.88 (d, 2H, C(6)H, C(8)H), 3.70 (s, 3H, OCH_3), 1.22 (d, 12H, [Q]CH_3), 3.24 (m, 2H, [Q]CH), 9.09 (s, 2H, [Q]NH_2^+); ^{13}C, δ 169.0 C(1), 114.2 C(2), 134.9 C(3), 131.1 C(4), 131.4 C(5) and C(9), 113.2 C(6) and C(8), 158.5 C(7), 54.9 C(OCH_3), 45.5 CH[HQ], 19.1 CH_3[HQ].

[HQ][Au(-*o*-hpspa)] (**19**). [Au(H-*o*-hpspa)] (0.06 g, 0.17 mmol), diisopropylamine (0.027 cm^3, 0.17 mmol), ethanol (7 cm^3), pale orange solid. Yield: 70%; mp: 192°C. (Found: C 36.3, H 4.2, S 6.6, N 2.6%. Calc. for $C_{15}H_{22}O_3SNAu$: C 36.5, H 4.5, S 6.5, N 2.8%). IR (cm^{-1}): 1,600 vs, $\nu(NH_2^+)$; 1,558 vs, $\nu_{asym}(CO_2^-)$; 1,350 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.70 (s, 1H, C(3)H), 8.52 (s, 1H, C(5)OH), 6.86 (d, 1H, C(6)H), 7.05 (pst, 1H, C(7)H), 6.68 (pst, 1H, C(8)H), 7.87 (d, 1H, C(9)H), 3.21 (d, 12H, [Q]CH_3), 1.20 (m, 2H, [Q]CH); ^{13}C, δ 171.3 C(1), 122.3 C(2), 136.6 C(3), 128.2 C(4), 155.7 C(5), 115.0 C(6), 131.3 C(7), 118.6 C(8), 131.5 C(9), 45.5 CH[HQ], 18.7 CH_3[HQ].

[HQ][Au(-*p*-hpspa)] (**20**). [Au(H-*p*-hpspa)] (0.05 g, 0.11 mmol), diisopropylamine (0.016 cm^3 0.11 mmol), ethanol (6 cm^3), pale yellow solid. Yield: 82%; mp: 207°C. (Found: C 36.3, H 4.7, S 6.6, N 2.6%. Calc. for $C_{15}H_{22}O_3SNAu$: C 36.5, H 4.5, S 6.5, N 2.8%). IR (cm^{-1}): 1,606 vs, $\nu(NH_2^+)$; 1,558 vs, $\nu_{asym}(CO_2^-)$; 1,345 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.57 (s, 1H, C(3)H), 7.82 (d, 2H, C(5)H, C(9)H), 6.75 (d, 2H, C(6)H, C(8)H), 8.90 (s, 1H, C(7)OH), 3.27 (d, 12H, [Q]CH_3), 1.19 (m, 2H, [Q]CH), 9.60 (s, 2H, [Q]NH_2^+); ^{13}C, δ 171.2 C(1), 124.3 C(2), 129.0 C(4), 131.5 C(5) and C(9), 114.5 C(6) and C(8), 158.4 C(7), 45.5 CH[HQ], 20.0 CH_3[HQ].

[HQ][Au(-diBr-*o*-hpspa)] (**21**). [Au(H-diBr-*o*-hpspa)] (0.07 g, 0.20 mmol), diisopropylamine (0.03 cm^3 0.20 mmol), ethanol (8 cm^3), yellow solid. Yield: 76%; mp: 189°C. (Found: C 34.9, H 4.5, S 5.5, N 5.5%. Calc. for $C_{15}H_{20}O_3SBr_2NAu$: C 27.7, H 3.1, S 4.9, N 2.1%). IR (cm^{-1}): 1,605 s br, $\nu(NH_2^+)$; 1,566 vs br, $\nu_{asym}(CO_2^-)$; 1,347 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.67 (s, 1H, C(3)H), 0.80 (br, 1H, C(5)OH), 7.54 (s, 1H, C(7)H), 7.32 (s, 1H, C(9)H), 3.20 (d, 12H, [Q]CH_3), 1.13 (m, 2H, [Q]CH); ^{13}C, δ 171.6 C(1), 126.0 C(2), 135.6 C(3), 126.8 C(4), 155.3 C(5), 116.4 C(6), 136.3 C(7), 113.0 C(8), 132.8 C(9), 45.8 CH[HQ], 19.8 CH_3[HQ].

[HQ][Au(cpa)] (**22**). [Au(Hcpa)] (0.07 g, 0.18 mmol), diisopropylamine (0.028 cm^3 0.18 mmol), ethanol (8 cm^3), beige solid. Yield: 58%; mp: 172°C. (Found: C 34.3, H 5.1, S 6.8, N 3.2%. Calc. for $C_{13}H_{24}O_2SNAu$: C 34.3, H 5.3, S 7.0, N 3.1%). IR (cm^{-1}): 1,617 vs, $\nu(NH_2^+)$; 1,543 vs, $\nu_{asym}(CO_2^-)$; 1,357 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 2.57 (m, 2H, C(4)H_2), 1.65 (m, 2H, C(5)H_2), 1.65 (m, 2H, C(6)H_2), 2.57 (m, 2H, C(7)H_2), 3.22 (d, 12H, [Q]CH_3), 1.13 (m, 2H, [Q]CH); ^{13}C, δ 171.5 C(1), 133.2 C(2), 61.3 C(3), 37.2 C(4), 28.0 C(5), 26.1 C(6), 35.1 C(7), 45.5 CH[HQ], 19.2 CH_3[HQ].

Complexes of the type Na[Au(L)]·H_2O Complexes **23**–**33** were prepared by adding NaOH to a suspension of the appropriate [Au(HL)] complex in water. The mixture was stirred at room temperature for 24 h, the solution was passed through a folded filter paper (Whatman No. 42) and the solvent was evaporated at room temperature.

Na[Au(pspa)]·H_2O (**23**). [Au(Hpspa)] (0.05 g, 0.13 mmol), NaOH (0.005 g, 0.13 mmol), H_2O (5 cm^3), pale yellow solid. Yield: 55%; mp: 215°C. (Found: C 26.0, H 1.8, S 7.2%. Calc. for $C_9H_8O_3SAuNa$: C 26.0, H 1.9, S 7.7%). IR (cm^{-1}): 1,573 vs, $\nu_{asym}(CO_2^-)$; 1,368 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.58 (s, 1H, C(3)H), 7.85 (d, 2H, C(5)H, C(9)H), 7.34 (t, 2H, C(6)H, C(8)H), 7.15 (m, 1H, C(7)H); ^{13}C, δ 173.9 C(1), 127.2 C(2), 140.2 C(3), 133.8 C(4), 129.9 C(5) and C(9), 128.0 C(6) and C(8), 128.7 C(7).

Na[Au(fspa)]·H_2O (**24**). [Au(Hfspa)] (0.10 g, 0.27 mmol), NaOH (0.011 g, 0.27 mmol), H_2O (8 cm^3), brown solid. Yield: 67%; mp: 210°C (Dec.). (Found: C 20.1, H 1.8, S 7.8%. Calc. for $C_7H_8O_5SAuNa$: C 19.8, H 1.9, S 7.6%). IR (cm^{-1}): 1,596 vs, $\nu_{asym}(CO_2^-)$; 1,382 s, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.58 (s, 1H, C(3)H), 7.28 (d, 1H, C(5)H), 6.52 (t, 1H, C(6)H), 7.60 (d, 1H, C(7)H); ^{13}C, δ 172.4 C(1), 135.0 C(2), 121.8 C(3), 153.2 C(4), 111.8 C(5), 111.4 C(6), 141.7 C(7).

Na[Au(tspa)]·H_2O (**25**). [Au(Htspa)] (0.12 g, 0.31 mmol), NaOH (0.013 g, 0.31 mmol), H_2O (10 cm^3), brown solid. Yield: 68%; mp: 221°C (Dec.). (Found: C 19.6, H 1.2, S 15.1%. Calc. for $C_7H_6O_3S_2AuNa$: C 19.9, H 1.4, S 15.2%). IR (cm^{-1}): 1,571 vs, $\nu_{asym}(CO_2^-)$; 1,368 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.78 (s, 1H, C(3)H), 7.35 (d, 1H, C(5)H), 7.04 (t, 1H, C(6)H), 7.45 (d, 1H, C(7)H); ^{13}C, δ 172.6 C(1), 125.2 C(2), 135.3 C(3), 142.2 C(4), 130.7 C(5), 126.3 C(6), 125.9 C(7).

Na[Au(-*o*-pyspa)]·H_2O (**26**). [Au(H-*o*-pyspa)] (0.05 g, 0.13 mmol), NaOH (0.005 g, 0.13 mmol), H_2O (5 cm^3), brown solid. Yield: 48%; mp: 224°C. (Found: C 22.8, H 1.7, S 7.9, N 3.2%. Calc. for $C_8H_7O_3SNAuNa$: C 23.0, H 1.7, S 7.7, N 3.3%). IR (cm^{-1}): 1,574 vs, $\nu_{asym}(CO_2^-)$; 1,381 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.10 (s, 1H, C(3)H), 7.58 (d, 1H, C(5)H), 7.81 (pst, 1H, C(6)H), 7.19 (pst, 1H, C(7)H), 8.56 (d, 1H, C(8)H); ^{13}C, δ 172.5 C(1), 135.9 C(2), 133.4 C(3), 153.2 C(4), 139.6 C(5), 29.2 C(6), 121.6 C(7), 125.6 C(8).

Na[Au(Clpspa)]·H_2O (**27**). [Au(HClpspa)] (0.10 g, 0.24 mmol), NaOH (0.01 g, 0.24 mmol), H_2O (8 cm^3), yellow solid. Yield: 60%; mp: 227°C. (Found: C 23.8, H 1.4, S 7.0%. Calc. for $C_9H_7O_3SClAuNa$: C 24.0, H 1.6, S 7.1%). IR (cm^{-1}): 1,589 vs, 1,575 vs, $\nu_{asym}(CO_2^-)$; 1,384 vs, 1,367 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.70 (s, 1H, C(3)H), 7.42 (d, 1H, C(6)H), 7.19 (t, 1H, C(7)H), 7.31 (t, 1H, C(8)H), 7.90 (d, 1H, C(9)H); ^{13}C, δ 172.3 C(1), 127.0 C(2), 133.2 C(3), 138.1 C(4), 135.2 C(5), 129.5 C(6), 129.9 C(7), 126.2 C(8), 128.2 C(9).

Na[Au(-*o*-mpspa)]·H_2O (**28**). [Au(H-*o*-mpspa)] (0.10 g, 0.25 mmol), NaOH (0.01 g, 0.25 mmol), H_2O (8 cm^3), yellow solid. Yield: 63%; mp: 220°C (Dec.). (Found: C 27.1, H 2.3, S 7.2%. Calc. for $C_{10}H_{10}O_4SAuNa$: C 26.9, H 2.3, S 7.2%). IR (cm^{-1}): 1,566 vs, $\nu_{asym}(CO_2^-)$; 1,372 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.73 (s, 1H, C(3)H), 8.00 (d, 1H, C(6)H), 6.89 (t, 1H, C(7)H), 7.16 (t, 1H, C(8)H), 7.91 (d, 1H, C(9)H), 3.72 (s, 3H, OCH_3); ^{13}C, δ 173.3 C(1), 127.6 C(2), 137.5 C(3), 125.5 C(4), 156.4 C(5), 110.2 C(6), 130.7 C(7), 119.3 C(8), 129.2 C(9), 55.3 C(OCH_3).

Na[Au(-*p*-mpspa)]·H_2O (**29**). [Au(H-*p*-mpspa)] (0.08 g, 0.2 mmol), NaOH (0.01 g, 0.2 mmol), H_2O (6 cm^3), orange solid. Yield: 68%; mp: 209°C (Dec.). (Found: C 26.7, H 2.1, S 6.9%. Calc. for $C_{10}H_{10}O_4SAgNa$: C 26.9, H 2.3, S 7.2%). IR (cm^{-1}): 1,570 s, $\nu_{asym}(CO_2^-)$; 1,383 s, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.56 (s, 1H, C(3)H), 7.93 (d, 2H, C(5)H), (C(9)H), 6.87 (d, 2H, C(6)H, C(8)H), 3.72 (s, 3H, OCH_3); ^{13}C, δ 173.4 C(1), 115.0 C(2), 134.5 C(3), 130.4 C(4), 131.2 C(5) and C(9), 113.3 C(6) and C(8), 158.7 C(7), 54.9 C(OCH_3).

Na[Au(-*o*-hpspa)]·H_2O (**30**). [Au(H-*o*-hpspa)] (0.06 g, 0.15 mmol), NaOH (0.006 g, 0.15 mmol), H_2O (5 cm^3), orange solid. Yield: 66%; mp: 225°C (Dec.). (Found: C 24.7, H 1.8, S 7.0%. Calc. for $C_9H_8O_4SAuNa$: C 25.0, H 1.9, S 7.4%). IR (cm^{-1}): 1,566 vs, $\nu_{asym}(CO_2^-)$; 1,363 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.84 (s, 1H, C(3)H), 9.63 (s, 1H, C(5)OH), 6.79 (m, 2H, C(6)H and C(8)H), 7.00 (pst, 1H, C(7)H), 8.10 (d, 1H, C(9)H); ^{13}C, δ 173.6 C(1), 123.9 C(2), 132.8 C(3), 155.3 C(5), 114.8 C(6), 130.4 C(7), 118.0 C(8), 129.8 C(9).

Na[Au(-*p*-hpspa)]·H_2O (**31**). [Au(H-*p*-hpspa)] (0.08 g, 0.2 mmol), NaOH (0.008 g, 0.2 mmol), H_2O (6 cm^3), orange solid. Yield: 60%; mp: 217°C (Dec.). (Found: C 24.8, H 2.1, S 7.2%. Calc. for $C_9H_8O_4SAuNa$: C 25.0, H 1.9, S 7.4%). IR (cm^{-1}): 1,563 vs, $\nu_{asym}(CO_2^-)$; 1,360 vs, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.56 (s, 1H, C(3)H), 7.87 (d, 2H, C(5)H, C(9)H), 6.71 (d, 2H, C(6)H, C(8)H), 9.50 (s, 1H, C(7)OH); ^{13}C, δ 172.6 C(1), 122.2 C(2),127.9 C(4), 131.5 C(5) and C(9), 114.8 C(6) and C(8), 156.3 C(7).

Na[Au(-diBr-*o*-hpspa)]·H_2O (**32**). [Au(H-diBr-*o*-hpspa)] (0.05 g, 0.09 mmol), NaOH (0.007 g, 0.09 mmol), H_2O (5 cm^3), yellow solid. Yield: 48%; mp: 219°C. (Found: C 17.9, H 1.1, S 5.2%. Calc. for $C_9H_6O_4SBr_2AuNa$: C 18.3, H 1.0, S 5.4%). IR (cm^{-1}): 1,565 vs br, $\nu_{asym}(CO_2^-)$; 1,361 vs br, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 7.90 (s, 1H, C(3)H), 7.75 (d, 1H, C(7)H), 7.20 (d, 1H, C(9)H); ^{13}C, δ 172.8 C(1), 125.6 C(2), 133.8 C(3), 126.3 C(4), 155.6 C(5), 115.9 C(6), 137.2 C(7), 112.5 C(8), 130.2 C(9).

Na[Au(cpa)]·H_2O (**33**). [Au(Hcpa)] (0.1 g, 0.28 mmol), NaOH (0.012 g, 0.28 mmol), H_2O (8 cm^3), brown solid. Yield: 68%; mp: 222°C. (Found: C 21.5, H 2.8, S 8.2%. Calc. for $C_7H_{10}O_3SAuNa$: C 21.3, H 2.6, S 8.1%). IR (cm^{-1}): 1,570 vs, $\nu_{asym}(CO_2^-)$; 1,387 vs br, $\nu_{sym}(CO_2^-)$. NMR (DMSO-d_6): ^1H, δ 2.65 (m, 2H, C(4)H_2), 1.56 (m, C(5)H_2), 1.56 (m, C(6)H_2), 2.36 (m, 2H, C(7)H_2); ^{13}C, δ 172.0 C(1), 129.6 C(2), 160.3 C(3), 38.2 C(4), 26.1 C(5), 24.8 C(6), 36.0 C(7).

Results and discussion

Synthesis and characterization

Complexes were prepared as described in the "Experimental" section. The [Au(HL)] complexes were obtained in high yields (close to 80% in most cases), whereas the reactions that afforded [HQ][Au(L)] and Na[Au(L)]·H_2O gave lower yields. The three types of compound differ in solubility. The [HQ][Au(L)] complexes are soluble in ethanol, methanol, acetone, chloroform and DMSO, the Na[Au(L)] H_2O complexes are soluble in water and DMSO, and the [Au(HL)] complexes are only soluble in DMSO.

The IR spectra of [Au(HL)] complexes do not show the ν(SH) band present at around 2,550 cm^{-1} in the spectra of the free ligands. Furthermore, the vibrations of the COOH group are slightly shifted from their positions in the spectra of the free ligands [14, 15]. These features suggest that, as in other complexes in which the COOH group is present, this group is not deprotonated and remains uncoordinated, with the complexes probably being polymeric species supported by Au–S bonds, as previously suggested for equivalent silver complexes [14, 15, 39, 40].

In the case of [HQ][Au(L)], the common features for the complexes are the absence of the ν(SH) band and of the bands due to the COOH group; both of these observations are consistent with the bideprotonation of the ligand in all cases. The existence of the diisopropylammonium cation is confirmed by the presence, at around 1,600 cm^{-1}, of a band due to the NH_2^+ group [41], which was previously identified in equivalent complexes with the same ligands [14, 15]. The $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$ bands are located in similar positions in the spectra of all the complexes, suggesting the same coordination mode for the carboxylate group, which, in all cases, acts as a monodentate group that is hydrogen bonded to the HQ cations [14, 15, 42]

The IR spectra of Na[Au(L)]·H_2O complexes do not contain the ν(SH) band or the bands due to the COOH group. The positions of the $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$ bands are again similar in all of the complexes and these positions are again compatible with the same kind of

monodentate coordination mode for the carboxylate group, which, in these cases, can be hydrogen bonded to the H_2O molecule instead of the diisopropylammonium cation.

NMR studies

For complexes of the type [Au(HL)] (**1**–**11**), the broad signal at around 13 ppm in the ^{1}H NMR spectra of the ligands persists, an observation consistent with the presence of the protonated COOH group. This signal is not present in the spectrum of the [Au(H-*o*-pyspa)] complex, probably due to an interchange with the deuterium of the solvent. In the ^{1}H spectrum of H_2-*o*-pyspa the presence of a broad singlet at 17.85 ppm is consistent with protonation of the pyridine nitrogen, which, together with the presence of only one proton on C(3)H, suggests that this compound is in the thione form in solution and not in the enethiol form. Coordination to gold causes significant changes in the ^{1}H NMR spectrum; the signal attributed to N–H does not appear for the complex, a fact that reflects deprotonation of this group and the evolution of the ligand to the thiol form. The ^{13}C NMR spectra of these complexes show the C(3) signal shifted to higher field with respect to that in the free ligand [14, 15], suggesting that the S-coordination found in the solid state, as in other complexes with these ligands [43, 44], is retained in solution.

For [HQ][Au(L)] (**12**–**22**) and Na[Au(L)]·H_2O (**23**–**33**) compounds the ^{1}H NMR spectra show a shift in the ligand C(3)H signal to higher field on complexation, which again suggests the persistence of the S–Au bond in solution; the disappearance of the broad signal located at around 13 ppm in the spectra of each free acid evidences the deprotonation of the COOH group in the complexes. The persistence of the S-coordination was confirmed by the shift in the C(3) signal in the ^{13}C NMR spectra. In these spectra, the C(1) peaks are in positions close to those found in compounds with a coordinated carboxylate group [45, 46] and, in particular, in the equivalent silver complexes [14, 15].

Antimicrobial activity

Antibacterial and antifungal activities are listed in Tables 1 and 2, as estimated by minimum inhibitory concentration (MIC; microgrammes per millilitre) and minimum bactericidal concentration (MBC; microgrammes per millilitre). Remarkable activity was not exhibited by either diisopropylammonium chloride [42], the ligands or complexes of the type [Au(HL)] (**1**–**11**), which in the case of the complexes can be attributed to the low solubility.

The majority of these new complexes showed better activity against the Gram (+) bacteria *S. aureus* and *B. subtilis* than against the Gram (−) *E. coli* and *P. aeruginosa* (the lower activity is shown against this latter bacterium even though the values are similar to those for *E. coli*). However, there are differences between the two classes of compounds and also between the compounds included in the [HQ][Au(L)] or Na[Au(L)]·H_2O classes.

Among the HQ derivatives, which in general are more active than the Na derivatives, [HQ][Au(fspa)] (**13**), [HQ][Au(-*o*-pyspa)] (**15**) and [HQ][Au(-diBr-*o*-hpspa)] (**21**) show higher activity against the Gram (+) bacteria; however, the wider spectrum of activity within this class corresponds to [HQ][Au(tspa)] (**14**), which shows significant activity against the assayed Gram (+) and Gram (−) bacteria.

Among the Na derivatives, the worst values were measured for Na[Au(cpa)]·H_2O (**33**), which showed a low activity against all the tested bacteria, whereas Na[Au(Clpspa)]·H_2O (**27**) showed significant activity against all the bacteria; furthermore, Na[Au(pspa)]·H_2O (**23**) showed better activity against the Gram (−) bacteria and Na[Au(-*o*-hpspa)]·H_2O (**30**) and Na[Au(-diBr-*o*-hpspa)]·H_2O (**32**) showed good values against the two Gram (+) bacteria and *E. coli*.

In an attempt to assess the bactericidal or bacteriostatic activity of these compounds, we also determined the MBC values for most of the synthesised compounds (Table 2). In the range of concentrations studied, we found bactericidal activity for some complexes and, as can be seen in Table 2, this activity is particularly relevant against *E. coli* and *B. subtilis*.

In the first case, among the HQ complexes, [HQ][Au(pspa)] (**12**), [HQ][Au(fspa)] (**13**), [HQ][Au(-*o*-hpspa)] (**19**) and [HQ][Au(-*p*-hpspa)] (**20**) showed only bacteriostatic activity. The complexes [HQ][Au(tspa)] (**14**), [HQ][Au(-*o*-pyspa)] (**15**), [HQ][Au(Clpspa)] (**16**), [HQ][Au(-diBr-*o*-hpspa)] (**21**) and [HQ][Au(cpa)] (**22**) showed bactericidal activity but only at concentrations higher than those at which the initial growth inhibition was observed; for [HQ][Au(-*o*-mpspa)] (**17**) and [HQ][Au(-*p*-mpspa)] (**18**), the bacteriostatic and bactericidal activity was observed at the same concentration.

Bactericidal activity was not observed for the Na complexes Na[Au(fspa)]·H_2O (**24**), Na[Au(tspa)]·H_2O (**25**), Na[Au(-*o*-mpspa)]·H_2O (**28**), Na[Au(-*o*-hpspa)]·H_2O (**30**), Na[Au(-*p*-hpspa)]·H_2O (**31**), Na[Au(-diBr-*o*-hpspa)]·H_2O (**32**) and Na[Au(cpa)]·H_2O (**33**), whereas this activity was observed for Na[Au(pspa)]·H_2O (**23**), Na[Au(-*o*-pyspa)]·H_2O (**26**), Na[Au(Clpspa)]·H_2O (**27**) and Na[Au(-*p*-mpspa)]·H_2O (**29**) at slightly higher concentrations than those at which the bacteriostatic activity was observed.

The wider expression of activity over the range of concentrations tested was identified against *B. subtilis*. With the exception of Na[Au(fspa)]·H_2O (**24**), Na[Au(-*o*-mpspa)]·H_2O (**28**) and Na[Au(cpa)]·H_2O (**33**), all of the complexes showed bactericidal activity—albeit at higher concentrations than those at which bacteriostatic activity was observed. In any case, none of the microorganisms tested showed tolerance to these products because the MIC/MBC ratio was less than 32 in all cases.

Table 1 Antimicrobial activities (MICs) of the complexes

Compound	*E. coli*	*S. aureus*	*B. subtilis*	*P. aeruginosa* ATCC 27853	*P. aeruginosa* Resistant	*C. albicans*
[HQ][Au(pspa)] (**12**)	25	25	25	50	25	50
[HQ][Au(fspa)] (**13**)	100	<6.25	<6.25	100	100	50
[HQ][Au(tspa)] (**14**)	25	12.5	25	12.5	12.5	100
[HQ][Au(-*o*-pyspa)] (**15**)	50	12.5	<6.25	25	50	200
[HQ][Au(Clpspa)] (**16**)	50	12.5	12.5	50	50	25
[HQ][Au(-*o*-mpspa)] (**17**)	50	12.5	25	25	25	50
[HQ][Au(-*p*-mpspa)] (**18**)	50	12.5	25	25	25	50
[HQ][Au(-*o*-hpspa)] (**19**)	50	50	25	50	50	>200
[HQ][Au(-*p*-hpspa)] (**20**)	50	12.5	100	50	50	200
[HQ][Au(-diBr-*o*-hpspa)] (**21**)	50	12.5	<6.25	50	50	50
[HQ][Au(cpa)] (**22**)	50	12.5	12.5	50	50	200
Na[Au(pspa)]·H_2O (**23**)	25	50	50	25	12.5	>200
Na[Au(fspa)]·H_2O (**24**)	100	12.5	200	100	100	200
Na[Au(tspa)]·H_2O (**25**)	50	25	50	100	100	200
Na[Au(-*o*-pyspa)]·H_2O (**26**)	25	12.5	50	100	100	200
Na[Au(Clpspa)]·H_2O (**27**)	12.5	12.5	12.5	25	12.5	>200
Na[Au(-*o*-mpspa)]·H_2O (**28**)	25	25	25	100	100	100
Na[Au(-*p*-mpspa)]·H_2O (**29**)	50	25	50	50	50	>200
Na[Au(-*o*-hpspa)]·H_2O (**30**)	<6.25	<6.25	12.5	50	50	100
Na[Au(-*p*-hpspa)]·H_2O (**31**)	50	50	25	50	50	>200
Na[Au(-diBr-*o*-hpspa)]·H_2O (**32**)	12.5	<6.25	<6.25	50	50	200
Na[Au(cpa)]·H_2O (**33**)	>200	>200	>200	>200	>200	>200

Minimum inhibitory concentration (microgrammes per millilitre)

Only three compounds showed bactericidal activity against *S. aureus*, and these were [HQ][Au(fspa)] (**13**), [HQ][Au(-diBr-*o*-hpspa)] (**21**) and Na[Au(-diBr-*o*-hpspa)]·H_2O (**32**); interestingly, for [HQ][Au(fspa)] (**13**) and [HQ][Au(-diBr-*o*-hpspa)] (**21**), bactericidal activity was detected at low concentrations, indicating a lack of tolerance to these compounds.

Against *P. aeruginosa*, only three HQ derivatives, [HQ][Au(tspa)] (**14**), [HQ][Au(Clpspa)] (**16**) and [HQ]

Table 2 MBC values for the complexes

Compound	*E. coli*	*S. aureus*	*B. subtilis*	*P. aeruginosa* ATCC 27853	*P. aeruginosa* Resistant
[HQ][Au(pspa)] (**12**)			50		
[HQ][Au(fspa)] (**13**)		6.25	50		
[HQ][Au(tspa)] (**14**)	100		100	50	
[HQ][Au(-*o*-pyspa)] (**15**)	100		50		
[HQ][Au(Clpspa)] (**16**)	100		25	100	
[HQ][Au(-*o*-mpspa)] (**17**)	50		50		
[HQ][Au(-*p*-mpspa)] (**18**)	50		100	100	
[HQ][Au(-diBr-*o*-hpspa)] (**21**)	100	12.5	6.25		
[HQ][Au(cpa)] (**22**)	100		50		
Na[Au(pspa)]·H_2O (**23**)	50		100	100	200
Na[Au(tspa)]·H_2O (**25**)			100		
Na[Au(-*o*-pyspa)]·H_2O (**26**)	200		200	200	
Na[Au(Clpspa)]·H_2O (**27**)	50		50	100	50
Na[Au(-*p*-mpspa)]·H_2O (**29**)	100		100		
Na[Au(-diBr-*o*-hpspa)]·H_2O **(32)**		25	12.5	200	200

Minimum bactericidal concentration (microgrammes per millilitre)

[Au(-*p*-mpspa)] (**18**), and four Na derivatives, Na[Au(pspa)]·H_2O (**23**), Na[Au(-*o*-pyspa)]·H_2O (**26**), Na[Au(Clpspa)]·H_2O (**27**) and Na[Au(-diBr-*o*-hpspa)]·H_2O (**32**), showed bactericidal activity; the same situation

Table 3 Antimicrobial activities (MICs) of the complexes prepared in this work and other compounds containing Ag–S bonds

Compound	*E. coli*	*S aureus*	*B. subtilis*	*P. aeruginosa*	*Resistant P. aeruginosa*	*C. albicans*
[HQ][Au(pspa)] (**12**)[a]	25	25	25	50	25	50
[HQ][Ag(pspa)][b]	200	100	50	25	25	50
[HQ][Au(fspa)] (**13**)[a]	100	<6.25	<6.25	100	100	50
[HQ][Ag(fspa)][b]	200	50	50	25	25	50
[HQ][Au(tspa)] (**14**)[a]	25	12.5	25	12.5	12.5	100
[HQ][Ag(tspa)][b]	>200	200	100	100	50	50
[HQ][Au(-*o*-pyspa)] (**15**)[a]	50	12.5	<6.25	25	50	200
[HQ][Ag(-*o*-pyspa)] [b]	200	200	100	100	100	100
[HQ][Au(Clpspa)] (**16**)[a]	50	12.5	12.5	50	50	25
[HQ][Ag(Clpspa)][c]	200	50	50	25	25	100
[HQ][Au(-*o*-mpspa)] (**17**)[a]	50	12.5	25	25	25	50
[HQ][Ag(-*o*-mpspa)][c]	100	50	50	12.5	25	25
[HQ][Au(-*p*-mpspa)] (**18**)[a]	50	12.5	25	25	25	50
[HQ][Au(-*o*-hpspa)] (**19**)[a]	50	50	25	50	50	>200
[HQ][Ag(-*o*-hpspa)][c]	200	100	25	25	>200	25
[HQ][Au(-*p*-hpspa)] (**20**)[a]	50	12.5	100	50	50	200
[HQ][Ag(-*p*-hpspa)][c]	200	100	25	25	>200	25
[HQ][Au(-diBr-*o*-hpspa)] (**21**)[a]	50	12.5	<6.25	50	50	50
[HQ][Ag(-diBr-*o*-hpspa)][c]	200	100	25	50	25	100
[HQ][Au(cpa)] (**22**)[a]	50	12.5	12.5	50	50	200
[HQ][Ag(cpa)][b]	>200	>200	100	200	100	200
Na[Au(pspa)]·H_2O (**23**)[a]	25	50	50	25	12.5	>200
Na[Ag(pspa)]·H_2O[b]	>200	25	25	50	25	50
Na[Au(fspa)]·H_2O (**24**)[a]	100	12.5	200	100	100	200
Na[Ag(fspa)]·H_2O[b]	100	25	12.5	25	6.25	50
Na[Au(tspa)]·H_2O (**25**)[a]	50	25	50	100	100	200
Na[Ag(tspa)]·H_2O[b]	100	25	25	50	25	100
Na[Au(-*o*-pyspa)]·H_2O (**26**)	25	12.5	50	100	100	200
Na[Au(Clpspa)]·H_2O (**27**)[a]	12.5	12.5	12.5	25	12.5	>200
Na[Ag(Clpspa)]·H_2O[c]	>200	12.5	12.5	50	12.5	>200
Na[Au(-*o*-mpspa)]·H_2O (**28**)[a]	25	25	25	100	100	100
Na[Ag(-*o*-mpspa)]·H_2O[c]	>200	12.5	12.5	50	12.5	50
Na[Au(-*p*-mpspa)]·H_2O (**29**)[a]	50	25	50	50	50	>200
Na[Au(-*o*-hpspa)]·H_2O (**30**)[a]	<6.25	<6.25	12.5	50	50	100
Na[Ag(-*o*-hpspa)]·$2H_2O$[c]	200	200	100	200	200	>200
Na[Au(-*p*-hpspa)]·H_2O (**31**)[a]	50	50	25	50	50	>200
Na[Ag(-*p*-hpspa)]·$2H_2O$[c]	100	>200	6.25	50	25	50
Na[Au(-diBr-*o*-hpspa)]·H_2O (**32**)[a]	12.5	<6.25	<6.25	50	50	200
Na[Ag(-diBr-*o*-hpspa)]·$2H_2O$[c]	>200	50	200	>200	>200	>200
Na[Au(cpa)]·H_2O (**33**)[a]	>200	>200	>200	>200	>200	>200
Na[Ag(cpa)]·H_2O[b]	>200	50	>200	>200	>200	50

Minimum inhibitory concentration (microgrammes per millilitre)

[a] This work

[b] Ref. [14]

[c] Ref. [15]

was found for the resistant strain of this bacterium, but in this case, only Na[Au(pspa)]·H_2O (**23**), Na[Au(Clpspa)]·H_2O (**27**) and Na[Au(-diBr-*o*-hpspa)]·H_2O (**32**) showed bactericidal activity.

The MIC values for the silver complexes shown in Table 3 enable a comparison of the activity between silver and gold complexes that incorporate the same ligand. It is interesting to underline the better activity of some gold compounds against *E. coli*, a Gram(−) bacterium that shows a low sensitivity to the previously prepared silver complexes.

The behaviour outlined above, with some exceptions—in particular for the Na derivatives—was also observed against the two Gram(+) bacteria but it did not persist against *P. aeruginosa* and the carbapenem-resistant *P. aeruginosa*. In these cases, the silver complexes generally showed better values than the gold complexes, as also shown against *C. albicans*.

If we consider the HQ and Na derivatives together and analyse the effect of the introduction of Au instead of Ag while maintaining the same ligand, the most marked effect was observed for -*o*-hpspa and diBr-*o*-hpspa, both ligands for which the phenyl group on the C(3) of the sulfanylpropenoic acid contains an –OH substituent in the ortho position.

Different activities were also previously found for equivalent Ag and Au complexes with P-donor [28], S-donor[13] or N-donor ligands [47]. As an interesting example in the latter case, it was shown [47] that [1-benzyl-3-*tert*-butylimidazol-2-ylidene]AuCl has significant activity against *B. subtilis* and that this activity is higher than that of the equivalent silver complex. Incubation of *B. subtilis* cells with the gold complex increased the cell length, indicating that this compound inhibits bacterial proliferation by blocking cytokinesis. In contrast, only a very small increase in cell length was observed under equivalent incubation with the silver complex. A different mode of antimicrobial action for equivalent silver and gold complexes was also previously proposed by Nomiya et al. [13, 28].

Conclusion

In summary, compounds of the type [Au(HL)], [HQ][Au(L)] and Na[Au(L)]·H_2O (where HQ=diisopropylammonium and H_2L are various sulfanylcarboxylates) have been synthesised and characterised. The low solubility of the compounds [Au(HL)] is probably the reason that they are inactive, but several compounds of the types [HQ][Au(L)] and Na[Au(L)]·H_2O show significant activity against the Gram(+) bacteria *S. aureus* and *B. subtilis.* The gold compounds generally show better activity than the silver analogues against *S. aureus* and *B. subtilis*, but low sensitivity against *E. coli*, *P. aeruginosa* and *C. albicans*. The results suggest a different mode of antimicrobial action for equivalent silver and gold compounds.

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