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Synthesis, characterization and X-ray crystal structure of $[Ag(Htsa)(PPh_3)_3]$ ($H_2tsa = o\text{-}HS(C_6H_4)CO_2H$). Comparison with $[Au(Htsa)(PPh_3)]$

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Abstract—A novel, monomeric triphenylphosphine silver(I) complex $[Ag(Htsa)(PPh_3)_3]$ ($H_2tsa = o\text{-}HS(C_6H_4)CO_2H$) was synthesized from three different ligand-exchange reactions, as **3** without any solvate or as **3a** with CH_2Cl_2 solvate, in good yield. The complex **3** can be interconverted with the previously obtained, two antimicrobially-active silver(I) thiosalicylates; one was the oligomeric, water-soluble complex $\{Na[Ag(tsa)] \cdot H_2O\}_n$, **1** ($n = 21$–$27$) and the other the polymeric, water-insoluble complex $[Ag(Htsa)]_n$, **2**. The analogous gold(I) complex $[Au(Htsa)(PPh_3)]$, **4**, was also isolated. The complexes **3**, **3a** and **4** were characterized with complete elemental analyses, TG/DTA, FT-IR and multinuclear NMR (^1H, ^{13}C, ^{31}P and ^{109}Ag) spectroscopies. The crystal structures of **3** and **4** were determined with single-crystal X-ray diffraction. The monomeric structure for **3** and the dimeric structure via hydrogen bonds of the carboxylic acid for **4** in the solid state were found.

Keywords: thiosalicylate; triphenylphosphine; silver(I) complex; gold(I) complex; X-ray crystal structure; NMR.

1. INTRODUCTION

In the medicinally or pharmaceutically active compounds of silver(I) and gold(I), most of the complexes formed with thiol and nitrogen-containing heterocyclic ligands are harder to crystallize and are believed to be polymeric [1–43]. In general, tertiary phosphine ligands have been usually employed in order to obtain crystalline compounds [23–35, 41, 42], although several crystalline thiolatogold(I) complexes without tertiary phosphines such as $[Au(SR)_2]^{n-}$ (HSR = mercapto-group compound) have been recently found [17–22, 39]. Probably, a recent development of monomeric Au^I compounds composed of both thiol and tertiary phosphine ligands stems from a discovery of auranofin ((2,3,4,6-tetra-*O*-acetyl-β-1-thio-D-glucopyranosato-*S*)(triethylphosphine)gold(I)) [6–10, 14–16], which has been used in chemotherapy as an effective antiarthritic agent and also as a realized medicine of oral-administration, although its mechanism or mode of action is unclarified as yet [6–10]. On the other hand, for non-crystalline, polymeric metal–thiolate and metal–imidazolate compounds, only a few structural studies have been performed by synchrotron X-ray studies containing EXAFS, XANES, WAXS and DAS [11, 12] and by Rietveld analysis using powder X-ray diffraction data [44, 45].

Very recently, we have prepared a monomeric imidazolatotris(triphenylphosphine) silver(I) complex $[Ag(imd)(PPh_3)_3]$ (Himd = imidazole) [41] by a reaction of PPh_3 ligands in CH_2Cl_2 with a polymeric complex $[Ag(imd)]_n$ which has shown wide spectra of excellent antibacterial and antifungal activities [42]. This monomeric complex was neither obtained from reactions of precursors $[AgCl(PPh_3)_3]$ and $[AgCl(PPh_3)_2]_2$ with a free Himd ligand in the presence of NaOH nor of $[AgCl(PPh_3)_2]_2$ with sodium salt of

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imidazolate. On the contrary, the corresponding Au^{I} complex [Au(imd)(PPh_3)] was obtained from a reaction of the precursor [AuCl(PPh_3)] with the Himd ligand in the presence of NaOH.

Also, two types of thiosalicylatosilver(I) complexes have been recently found [38]; one was an oligomeric, water-soluble and yellow complex $\{Na[Ag(tsa)]\cdot H_2O\}_n$, **1** ($n = 21$–$27$; $H_2tsa = o$-$HS(C_6H_4)CO_2H$) and the other a polymeric, water-insoluble and orange complex $[Ag(Htsa)]_n$, **2**, both of which have displayed effective antimicrobial activities against selected bacteria, yeast and molds. The present work has been aimed at (i) preparing a monomeric form of the thiosalicylatosilver(I) complex, e.g. [Ag(Htsa)(PPh_3)$_3$], **3**, through ligand-exchange reactions of polymeric complex **2** or of some precursor silver(I) complexes such as [AgCl(PPh_3)$_3$] and [AgCl(PPh_3)$_2$]$_2$, (ii) applying the same concept to gold(I) chemistry to obtain the thiosalicylatogold(I) complex, e.g. [Au(Htsa)(PPh_3)], **4**, (iii) providing X-ray crystal structures of **3** and **4** in the solid state and (iv) clarifying the behavior in solution of **3** and **4**. The X-ray crystal structures of several (arenethiolato)metal complexes have been determined such as [Au(Htsa)(PCy_3)] (PCy_3 = tricyclohexylphosphine) [26], [Cu($SC_6H_4NMe_2$-2)]$_3$, [Cu(S-1-$C_{10}H_6NMe_2$-8)]$_9$, [Cu$_3$(S-1-$C_{10}H_6NMe_2$-8)$_2$(C≡C^{t}Bu)]$_2$ [46], [Cu$_8${$SC_6H_3(CH_2NMe_2)_2$-2,6}$_3$Br$_5$] [47], [Mg{S(C_6H_4-2-CH_2NMe_2)}$_2$]$_2$ [48] and [Li{SC_6H_4((R)-CH(Me)NMe_2)-2}]$_6$ and [Li{$SC_6H_3(CH_2NMe_2)_2$-2,6}]$_6$ [49].

Herein we report the full details of the synthesis and characterization of the complexes [Ag(Htsa)(PPh_3)$_3$], **3**, in 37% yield and [Ag(Htsa)(PPh_3)$_3$]$\cdot CH_2Cl_2$, **3a**, in 52% yield both as colorless needle crystals, and [Au(Htsa)(PPh_3)], **4**, in 72% yield as pale yellow prism crystals. The X-ray crystal structures of **3** and **4** were determined by single-crystal X-ray diffraction. Also reported are the compositional characterization of **3**, **3a** and **4** by full elemental analyses, FT-IR, thermoglavimetric and differential thermal analyses (TG/DTA) and their structural characterization in solution by ^{1}H, ^{13}C and ^{31}P NMR spectroscopies, and additionally by solution ^{109}Ag NMR spectroscopy for **3**.

2. EXPERIMENTAL

2.1. *Materials*

All chemicals were reagent grade and were used as received: thiosalicylic acid (H_2tsa; *o*-mercaptobenzoic acid), $AgNO_3$, Na[$AuCl_4$]$\cdot 2H_2O$, $(C_6H_5)_3P$, NaOH, ethanol, acetone, diethyl ether, dichloromethane (all from Wako); $CDCl_3$, DMSO-d_6 (Aldrich); CD_2Cl_2 (Isotec). Several precursor complexes such as [AgCl(PPh_3)$_3$] [50], [AgCl(PPh_3)$_2$]$_2$ [51] and [AuCl(PPh_3)] [52–54] were prepared according to the literature, respectively. Polymeric, water-insoluble and orange complex $[Ag(Htsa)]_n$, **2**, was prepared as previously described [38].

2.2. *Instrumentation/analytical procedures*

Elemental analyses on samples dried overnight at room temperature under 10^{-3}–10^{-4} Torr were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). Infrared spectra were obtained on a JASCO FT-IR 300 spectrometer as KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Rigaku TG 8101D and TAS 300 data-processing system. TG/DTA measurements were run under air with a temperature ramp of 1°C/min between 20 and 500°C.

^{1}H NMR (399.65 MHz), ^{13}C NMR (100.4 MHz) and ^{31}P NMR (161.70 MHz) spectra were recorded at 22°C in 5 mm o.d. tubes on a JEOL JNM-EX 400 FT-NMR spectrometer with a JEOL EX-400 NMR data-processing system. ^{1}H and ^{13}C{^{1}H} NMR spectra of the complexes were measured in $CDCl_3$ with reference to an internal standard of tetramethylsilane (TMS). Chemical shifts are reported on the δ scale and resonances downfield of TMS (δ 0) are recorded as positive. ^{31}P{^{1}H} NMR spectra of the complexes were measured in $CDCl_3$ with reference to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. Chemical shifts are reported as negative for resonances upfield of H_3PO_4 (δ 0). The ^{31}P{^{1}H} NMR spectra at −90°C were measured in CD_2Cl_2 with an external standard of 25% H_3PO_4 by a substitution method.

The two-dimensional ^{1}H–^{13}C COSY NMR spectra and both two-dimensional NMR spectra of ^{1}H–^{13}C HMBC (heteronuclear multiple bond correlation) method by a correlation $^3J_{C-H}$ between ^{1}H and ^{13}C atoms separated by three bonds and ^{1}H–^{13}C HMQC (heteronuclear multiple quantum coherence) by a correlation between ^{1}H and ^{13}C which are directly spin–spin coupled, were measured in $CDCl_3$ solution, all spectra referenced to an internal TMS in 5 mm o.d. tubes using a JEOL JNM-EX 400 NMR spectrometer and JEOL EX-400 NMR data-processing system or using a VARIAN UNITY 500 FT-NMR spectrometer. Pulse sequences and spectral parameters for the HMBC and HMQC methods are reported elsewhere [55].

^{109}Ag NMR (18.45 MHz) spectra were recorded at 22°C in 10 mm o.d. tubes on a JEOL JNM-EX 400 FT-NMR spectrometer equipped with a JEOL NM-40T10L low-frequency tunable probe. The ^{109}Ag NMR spectra of the complexes were measured in $CDCl_3$ with reference to an external standard of saturated $AgNO_3$–D_2O solution by a substitution method. Chemical shifts are reported on the δ scale with resonances downfield of $AgNO_3$ (δ 0) as positive. Spectral parameters for ^{109}Ag NMR include: pulse width of

13.2 μs, acquisition time of 0.39 s, recycle time of 1.39 s and sweep width of 21,008 Hz.

2.3. *Preparation of the complexes*

[Ag(Htsa)(PPh_3)$_3$], **3**: From a reaction of [AgCl(PPh_3)$_2$]$_2$ with H_2tsa in the presence of NaOH. To 0.600 g (0.449 mmol) [AgCl(PPh_3)$_2$]$_2$ dissolved in 40 ml dichloromethane was added a clear yellow solution of 0.140 g (0.908 mmol) of H_2tsa and 0.036 g (0.900 mmol) of NaOH in 50 ml ethanol. The yellow–white suspension obtained was stirred for 30 min and filtered through a folded filter paper (Whatman No. 5). The clear filtrate was concentrated at 60°C to a volume of *ca*. 70 ml by rotary evaporation, followed by standing for a few days in a refrigerator at 5°C. Colorless needle crystals formed were collected on a membrane filter (JG 0.2 μm), washed with water (100 ml × 2), then with ethanol (100 ml × 2) and finally with 100 ml diethyl ether, and dried *in vacuo* for 2 h. Yield: 0.35 g (37.4%) of light- and thermally-stable, colorless needle crystals, which were soluble in chloroform and dichloromethane, sparingly soluble in DMSO, acetone and acetonitrile, but insoluble in water, ethanol and diethyl ether.

Found: H, 4.81; C, 70.00. Calc. for $H_{50}C_{61}O_2P_3SAg$ or [Ag(Htsa)(PPh_3)$_3$]: H, 4.81; C, 69.92. TG/DTA: no weight loss observed below 150°C; decomposition started around 150°C with an endothermic peak at 170°C. IR (KBr disk): *v* 1701vs, 1583m, 1479s, 1433vs, 1327m, 1309m, 1271m, 1217m, 1184w, 1157m, 1093m, 1026m, 997m, 742vs, 694vs, 515s, cm^{-1}. ^{1}H and ^{13}C NMR in $CDCl_3$ are shown in Table 3.

[Ag(Htsa)(PPh_3)$_3$]·CH_2Cl_2, **3a**: From a reaction of [AgCl(PPh_3)$_3$] with H_2tsa in the presence of NaOH. To 2.79 g (3.00 mmol) [AgCl(PPh_3)$_3$] dissolved in 60 ml dichloromethane was added a clear yellow solution of 0.463 g (3.00 mmol) of H_2tsa and 0.120 g (3.00 mmol) of NaOH in 180 ml ethanol. The yellow–white suspension obtained was stirred for 30 min and filtered through a folded filter paper (Whatman No. 5). The clear filtrate was concentrated at 60°C to a volume of *ca*. 200 ml by rotary evaporation, followed by standing for a few days in a refrigerator at 5°C. Colorless needle crystals formed were collected on a membrane filter (JG 0.2 μm), washed with water (100 ml × 2), then with ethanol (100 ml × 2) and finally with 100 ml diethyl ether and dried *in vacuo* for 2 h. Yield: 1.75 g (51.5%) of colorless needle crystals, which were soluble in chloroform and dichloromethane, sparingly soluble in DMSO, acetone and acetonitrile, but insoluble in water, ethanol and diethyl ether.

Found: H, 4.74; C, 65.91; O, 2.66; P, 8.10; S, 2.63; Cl, 5.75; Ag, 9.68; total 99.47%. Calc. for $H_{52}C_{62}O_2P_3SCl_2Ag$ or [Ag(Htsa)(PPh_3)$_3$]·CH_2Cl_2: H, 4.63; C, 65.74; O, 2.82; P, 8.20; S, 2.83; Cl, 6.26; Ag, 9.52. TG/DTA: weight loss of 6.82% observed below 117°C with an endothermic point at 110°C. Calc. for [Ag(Htsa)(PPh_3)$_3$]·$x$$CH_2Cl_2$, 7.50% ($x$ = 1); decomposition gradually started around 150°C. IR (KBr disk): *v* 1703vs, 1583m, 1479s, 1433vs, 1327m, 1309m, 1273m, 1221w, 1182w, 1157w, 1092s, 1026m, 999m, 742vs, 694vs, 513vs cm^{-1}. ^{1}H and ^{13}C NMR in $CDCl_3$ are shown in Table 3. ^{31}P NMR ($CDCl_3$): δ 4.55 (PPh_3). ^{109}Ag NMR ($CDCl_3$): δ 1196.

3a: From a reaction of polymer [Ag(Htsa)]$_n$ with PPh_3. To a yellow suspension of 0.522 g (2.00 mmol) of powder-solid [Ag(Htsa)]$_n$ in 40 ml ethanol was added a clear colorless solution of 1.57 g (6.00 mmol) of triphenylphosphine in 120 ml dichloromethane. Stirring continued for 3 h. During the initial 15 min-stirring, the solution became clear yellow. The clear filtrate obtained by passing through a folded filter paper (Whatman No. 2) was slowly evaporated at room temperature. A crude compound of pale yellow plate crystals formed within a few days was collected on a membrane filter (JG 0.2 μm), washed with ethanol (100 ml × 2) and then with diethyl ether (100 ml × 2) and dried *in vacuo* for 2 h. The yield of this crude product was 1.64 g.

To the crude product redissolved in 40 ml dichloromethane was added 40 ml ethanol, followed by filtering through a filter paper (Whatman No. 2) and the filtrate was slowly evaporated by standing for a few days at room temperature. Colorless needle crystals formed here were collected on a membrane filter (JG 0.2 μm), washed twice each with 100 ml ethanol and 100 ml diethyl ether and dried *in vacuo* for 2 h. Yield: 0.95 g (42.1%).

Found: H, 4.59; C, 65.94. Calc. for $H_{52}C_{62}O_2P_3SCl_2Ag$ or [Ag(Htsa)(PPh_3)$_3$]·CH_2Cl_2: H, 4.63; C, 65.74. TG/DTA: weight loss of 7.24% observed below 125°C with an endothermic peak at 104°C; Calc. for [Ag(Htsa)(PPh_3)$_3$]·$x$$CH_2Cl_2$, 7.50% ($x$ = 1); decomposition started around 150°C with an endothermic peak at 170°C. IR (KBr disk): *v* 1704vs, 1584m, 1478s, 1433vs, 1327w, 1308w, 1272m, 1222w, 1182w, 1157m, 1092s, 1027m, 998m, 742vs, 694vs, 512vs, cm^{-1}. ^{1}H and ^{13}C NMR in $CDCl_3$ are shown in Table 3. ^{31}P NMR ($CDCl_3$): δ 4.57 (PPh_3).

[Au(Htsa)(PPh_3)], **4**: This compound was prepared by a modification of the literature method [26], using 0.247 g (0.500 mmol) of [AuCl(PPh_3)], 0.077 g (0.500 mmol) of H_2tsa in 50 ml ethanol and 1 ml (0.500 mmol) of 0.5 M NaOH aqueous solution. Yield: 0.22 g (72.0%) of pale yellow cubic crystals with melting point 154–156°C, which were soluble in acetone, chloroform and benzene, sparingly soluble in ethanol, but insoluble in water and diethyl ether. This compound was light- and thermally-stable.

Found: H, 3.31; C, 48.92; O, 5.47; P, 5.19; S, 5.09; Au, 31.40; total 99.38%. Calc. for $H_{20}C_{25}O_2PSAu$ or [Au(Htsa)(PPh_3)]: H, 3.29; C, 49.03; O, 5.22; P, 5.06; S, 5.23; Au, 32.16. TG/DTA: negligible weight loss (0.3%) observed below 150°C with an endothermic peak at 163°C; decomposition began at 270°C. IR (KBr disk): *v* 1682vs, 1585m, 1477m, 1464m, 1433s, 1406m, 1309s, 1265m, 1248m, 1099s, 1053m, 1036m, 997w, 958w, 754s, 694s, 538s, 507s, 496s cm^{-1}. ^{1}H and

^{13}C NMR in $CDCl_3$ are shown in Table 3. ^{31}P NMR ($CDCl_3$) δ 37.56 (PPh_3).

2.4. *X-ray structural analysis*

Crystals of complex **3** were obtained as colorless needles from a solution of the solvent mixture, dichloromethane–ethanol, and those of **4** as pale yellow cubes from a solution of dichloromethane–acetone. During a few days' standing at room temperature, crystals of sufficient quality suitable for single-crystal X-ray diffraction studies were grown.

Each single-crystal of **3** and **4** was mounted on glass fiber and transferred to a Rigaku AFC5S diffractometer. Cell contents and orientation matrix of **3** and **4** were obtained from the least-squares refinement of 25 and 23 reflections, respectively. The reflection data were collected using ω–2θ scan with graphite-monochromated Mo–Kα radiation at room temperature. The intensities of three standard reflections which were measured after every 150 reflections remained constant throughout the data collection. The data were corrected for Lorentz and polarization effects and empirical absorption corrections based on PSI scan were applied to the data. For the overall averaged transmission curve, the transmission factors of **3** and **4** were in the range of 0.93–1.00 and 0.23–1.00, respectively. The structures were solved by direct methods followed by subsequent difference Fourier calculation and refined by a full-matrix least-squares procedure using TEXSAN package [56]. For **3**, all atoms except hydrogen and carbon were refined anisotropically. Carbon and hydrogen atoms were refined isotropically. For **4**, all atoms except hydrogen were refined anisotropically and hydrogen atoms isotropically.

Crystal data, data collection and refinement for **3** and **4** are summarized in Table 1.

3. RESULTS AND DISCUSSION

3.1. *Molecular formula and compositional characterization*

The composition and molecular formula of **3** which consists of one silver(I) atom, one coordinating $Htsa^-$ ligand and three PPh_3 ligands without any solvated molecules, those of **3a** with one solvated CH_2Cl_2 molecule and those of **4** composed of one gold(I) atom, one $Htsa^-$ ligand and one PPh_3 ligand without any solvated molecules are based on elemental analyses (in particular for **3a** and **4**, all elements including oxygen, 99.47 and 99.38% totals are observed; see Section 2), TG/DTA and single-crystal X-ray analyses described later.

As to the solvation by one CH_2Cl_2 molecule in **3a**, in the absence of any other sources of chlorine, the Cl analysis (calc. 6.26, found 5.75%) reflects the presence of solvated CH_2Cl_2. The additional evidence for the presence of solvated CH_2Cl_2 is provided by a proton signal at 5.27 ppm observed in ^1H NMR spectra and by a carbon signal at 53.42 ppm in ^{13}C NMR spectra. TG/DTA analyses of two independent samples prepared from different starting materials also confirm the presence of one solvated CH_2Cl_2 as the observed weight loss 6.82 and 7.24% (calc. 7.50%) with an endothermic peak at 110 and 104°C, respectively.

The solid FT-IR spectra (Fig. 1) of complexes **3** and **4** show a disappearance of the S–H stretching band around 2560 cm^{-1} due to the SH group in the free H_2tsa ligand, suggesting the metal–S bond formation. Also shown is that the carbonyl stretching bands around 1700 cm^{-1} are unchanged after complexation, compared with that of the free H_2tsa ligand, suggesting that the carboxyl group remains protonated and does not coordinate to the central metal ions. Many small bands observed in 3000–2500 cm^{-1} region are also attributed to the presence of a protonated carboxylic group as usually observed. Thus, the IR spectra of all complexes **3**, **3a** and **4** show that the coordination by the $Htsa^-$ ligand to metal centers is only through the sulfur atom in the mercapto group.

No coordination of the carboxyl oxygen atoms to the metal is also supported by the X-ray analysis described later. It has been also clarified by ESCA measurements of the two thiosalicylatosilver(I) complexes **1** and **2** that even the deprotonated carboxyl group does not participate in the coordination to the silver(I) atom [38].

3.2. *Synthetic reactions and ligand replacement*

The conceptually straightforward, synthetic reactions of thiosalicylatotris(triphenylphosphine)silver(I), which has been herein isolated as **3** without any solvate and/or as **3a** with CH_2Cl_2 solvate, are outlined in equations (1)–(3) (Scheme 1). On the other hand, the synthesis of thiosalicylato(triphenylphosphine)gold(I) obtained as **4** is shown in equation (6).

The reactions in equations (2) and (6) exhibit a simple ligand replacement of the coordinated Cl^- ligand with free H_2tsa without change in the coordination number of the starting silver(I) and gold(I) atoms. In the reaction shown in equation (1), the dimeric silver(I) structure with bridged Cl^- ligands is transformed to the monomeric structure by their ligand exchange with free H_2tsa, where the coordination number of silver(I) remains unchanged. In the reaction in equation (3), the polymeric structure with bridged sulfur atoms is changed to the monomeric structure accompanied with a change in the coordination number of the silver(I) atom from 2 to 4.

From the synthetic reactions in equations (1)–(3), the ease of ligand replacement, i.e. the relative ordering of ligand replacement, is suggested for the formation of the silver(I) complexes $[AgL(PPh_3)_n]_m$ from the starting complexes $[AgL]_x$ (L = N, S donor atoms) and $[AgCl(PPh_3)_n]_m$ to be: Ag–P $\gg$ Ag–S > Ag–Cl

Table 1. Summary of X-ray diffraction data

	3 [Ag(Htsa)(PPh_3)$_3$]	**4** [Au(Htsa)(PPh_3)]
Formula	$C_{61}H_{50}O_2P_3AgS$	$C_{25}H_{20}O_2PAuS$
MW	1047.91	612.43
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$ (#14)	$P\bar{1}$ (#2)
a (Å)	10.74(1)	11.542(3)
b (Å)	24.993(3)	12.091(4)
c (Å)	19.846(3)	8.750(3)
α (°)	90	97.85(3)
β (°)	105.30(4)	107.79(3)
γ (°)	90	102.44(3)
V (Å^3)	5136(6)	1108.2(7)
F(000)	2160	592.00
Z	4	2
$d_{calc.}$ (g · cm^{-1})	1.355	1.904
Crystal size (mm)	0.2 × 0.2 × 0.2	0.2 × 0.3 × 0.2
No. of reflections used for	25	23
Unit cell dimension (2θ range)	(30.1–33.0)	(30.2–34.5)
Radiation	Mo–Kα (λ = 0.71069 Å)	Mo–Kα (λ = 0.71069 Å)
Scan mode	2θ–ω	2θ–ω
Scan width	0.84 + 0.30 tan θ	1.63 + 0.30 tan θ
Scan speed (min^{-1})	16	32
2θ range	6–50	6–55
μ (cm^{-1})	5.69	68.16
Total reflections	7912	5351
Reflections unique	7392	5099
Reflections observed	2143 [$I > 2\sigma(I)$]	3223 [$I > 3\sigma(I)$]
R, R_w	0.086, 0.055	0.055, 0.041
GOF	1.58	1.89

$R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$, $R_w = [\Sigma(\omega\,[|F_o| - |F_c|]^2/\Sigma\omega(|F_o|)^2]^{1/2}$, with $\omega = 4F_o^2/[\sigma^2(F_o^2)]$.

and, from equation (6), that for the gold(I) complexes is also suggested to be: Au–P ≫ Au–S > Au–Cl. On the other hand, the synthetic reactions of the recently found, metal(I) complexes containing nitrogen-containing heterocycles such as imidazole and triazoles have indicated that the relative ordering for silver(I) follows Ag–P ≫ Ag–Cl > Ag–N ≫ Ag–O, while that for gold(I) follows: Au–P ≫ Au–N > Au–Cl ≫ Au–O [41–43]. Thus, we can deduce the relative ligand replacement for the silver(I) complexes as Ag–P ≫ Ag–S > Ag–Cl > Ag–N ≫ Ag–O, while that for the gold(I) complexes, i.e, as Au–P ≫ Au–S > Au–N > Au–Cl ≫ Au–O. This information allows us to know if target molecules by medicinally or pharmaceutically active compounds of silver(I) and gold(I) are proteins containing enzymes as N,O,S-donors or nucleic acids as N,O-donors of biological ligands. In fact, the wide spectra of excellent antibacterial and antifungal activities found in the [Ag(imd)]$_n$ (Himd = imidazole) has been attributed to proteins containing a sulfur donor atom as the potential target molecule for inhibition of growth of the test organisms, but not to nucleic acids without a sulfur donor [41, 42].

The proton attached to the carboxyl group in the present complexes **3** and **4** could not be exchanged with an alkali metal ion such as sodium ion; i.e. neither "Na[Ag(tsa)(PPh_3)$_3$]" nor "Na[Au(tsa)(PPh_3)]" can be derived by the reactions of aqueous NaOH with **3**, **3a** or **4**, respectively. We found, or rather, that the reactions of **3** and **3a** with aqueous NaOH resulted in reproducing the water-soluble, oligomeric species, {Na[Ag(tsa)]}$_n$ **1** by a loss of the PPh_3 ligands. Since the polymeric compound **2** can be converted to the oligomer **1** by its reaction with aqueous NaOH and **1** can also be transformed to **2** by its reaction with aqueous HCl [38], there exists an interconversion relationship between **3** and **2** via the oligomer **1** as a mediator as shown in equations (3)–(5) (Scheme 1).

3.3. *Molecular and crystal structures of* **3** *and* **4**

The molecular structures of **3** and **4** were determined with single-crystal X-ray diffraction analysis and are shown in Figs 2 and 3, respectively. Their selected distances and angles are listed in Table 2.

The silver atom of **3** is coordinated with three phosphorus atoms of the PPh_3 ligands and the sulfur atom of the $Htsa^-$ ligand to form a tetrahedral geometry.

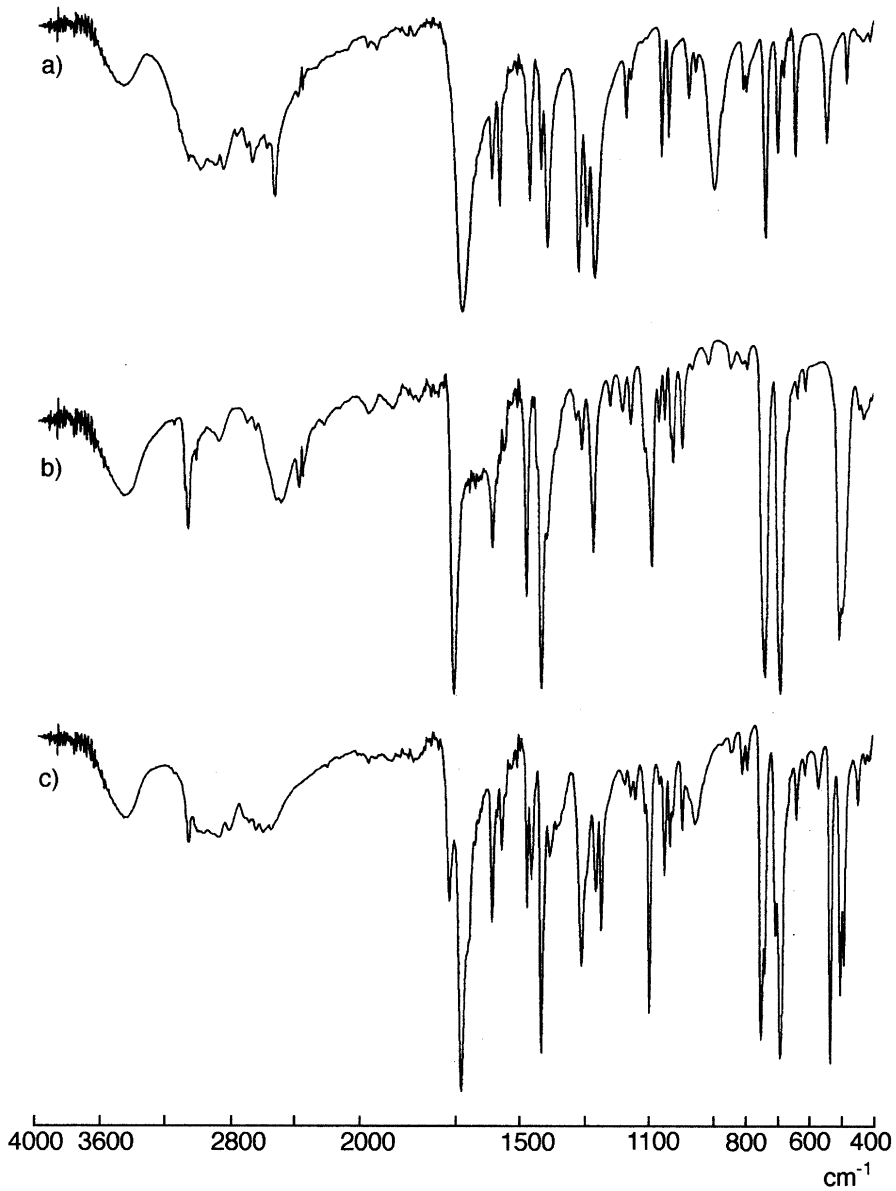


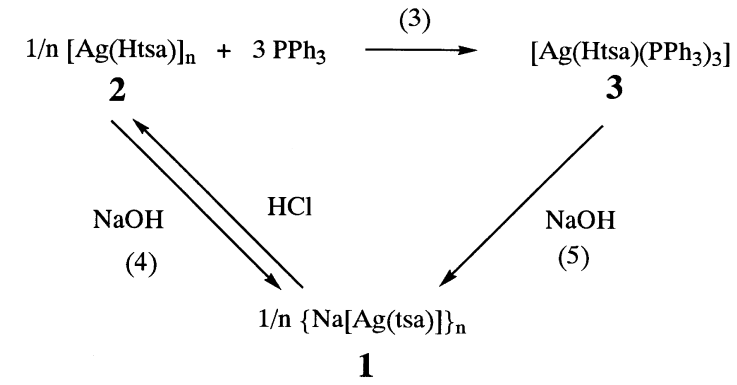
Fig. 1. Solid FT-IR spectra measured in KBr disks in the 4000–400 cm^{-1} region of (a) free H_2tsa ligand, of (b) [Ag(Htsa)$(PPh_3)_3$], **3**, and of (c) [Au(Htsa)(PPh_3)], **4**.

As found in Table 2, the angles around the silver atom deviate from the ideal value of 109.5°. One S–Ag–P angle is smaller and two of them are greater than 109.5°. All P–Ag–P angles are greater than 109.5°. The geometries around the silver atoms of the starting materials $[AgCl(PPh_3)_3]$ and $[AgCl(PPh_3)_2]_2$ are also tetrahedral [50, 51]. Three structures of the silver(I) complexes can be compared with each other. The distances and angles of **3** are similar to those of $[AgCl(PPh_3)_3]$, except longer Ag–S bond vs Ag–Cl bond, rather than those of $[AgCl(PPh_3)_2]_2$. The dihedral angle between the planes of the carboxyl group (A; O1, O2, C61) and the $Htsa^-$ (B; S1, C55, C56, C57, C58, C59, C60) is 176°, showing the $SC_6H_4CO_2H$ moiety of **3** planar. The dihedral angles between the plane C (Ag–S–C56) and the A or the B are 139° and 43°, respectively. The distances between the silver and oxygen atoms are 6.70 (Ag–O1), 6.84 (Ag–O1′) and 5.10 (Ag–O2) Å. These angles and distances indicate that the carboxyl group is directed away from the silver atom. From the intermolecular oxygen distances, no intermolecular hydrogen bond between the carboxyl groups of the $Htsa^-$ is observed for **3**. Thus, the complex **3** is monomeric.

The gold atom in **4** is placed in the linear geometry defined by the phosphorus atom of the PPh_3 ligand and the sulfur atom of the $Htsa^-$. The P–Au–S angle of **4** is smaller (173.0(1)°) than that of the recently

$$[AgCl(PPh_3)_2]_2 + H_2tsa + NaOH \xrightarrow{(1)} [Ag(Htsa)(PPh_3)_3] + AgCl + PPh_3 + NaCl + H_2O$$

$$[AgCl(PPh_3)_3] + H_2tsa + NaOH \xrightarrow{(2)} [Ag(Htsa)(PPh_3)_3] + NaCl + H_2O$$



$$[AuCl(PPh_3)] + H_2tsa + NaOH \xrightarrow{(6)} [Au(Htsa)(PPh_3)] + NaCl + H_2O$$

Scheme 1. Reaction schemes.

reported, related complex [Au(Htsa)(PCy_3)] (PCy_3 = tricylcohexylphosphine) (176.8°) [26]. The Au–S and the Au–P distances of 4 ((2.292(4), 2.260(3) Å) are slightly shorter than those of [Au(Htsa)(PCy_3)] (2.313(1), 2.271(1) Å) and they are equal within experimental errors to the distances of other gold(I) complexes with a PPh_3 ligand, [Au(2-tu)(PPh_3)] (2-Htu = 2-thiouracil) (Au–S 2.296(2) A; Au–P 2.300(2) Å) [30]. This picture may be attributed to the difference in cone-angles of the phosphine ligands. The dihedral angles of the carboxyl group (D; O2, O3, C4) and the $Htsa^-$ (E; S1, C5, C6, C7, C8, C9, C10) is 142°, indicating some delocalization of π-electron density occurs between the SC_6H_4 and CO_2H moieties. The dihedral angles of the planes of F (Au–S1–C10) and the D or the E are 48° and 138°, respectively. The Au–O3 distance of **4** is 3.21 Å, which is much shorter than that of [Au(Htsa)(PCy_3)] [26]. These angles and distances show that the carboxyl group is not directed away from the gold atom as seen in [Au(Htsa)(PCy_3)] (5.10 and 6.35 Å). The distance of O2–$O3^i$ of the $Htsa^-$ is 2.56(1) Å (a symmetry operation i; $-x$, $1-y$, $-z$), revealing that an intermolecular hydrogen bond is formed in **4**. This is contrasted with the structure of **3**. In **4**, two [Au(Htsa)(PPh_3)] units are centrosymmetrically associated via the carboxylic moieties to form a dimeric unit. This picture has also been shown in [Au(Htsa)(PCy_3)] [26].

3.4. *Solution NMR* (^{1}H, ^{13}C, ^{31}P *and* ^{109}Ag) *characterization*

The ^{31}P NMR spectra measured in $CDCl_3$ at 22°C show a single peak due to the coordinating PPh_3 ligands at 4.79 ppm for **3** [Fig. 4(a)], at 4.55–4.57 ppm for **3a** and at 37.56 ppm for **4** [Fig. 4(c)], while at −5.33 ppm for the free PPh_3 ligand. It is obvious that the coordination of the phosphorus donor atom to the metal center significantly influences the phosphorus resonance and the ^{31}P chemical shift also reflects a difference between silver(I) and gold(I) as the metal center.

On the other hand, the ^{31}P NMR [Fig. 4(b)] at

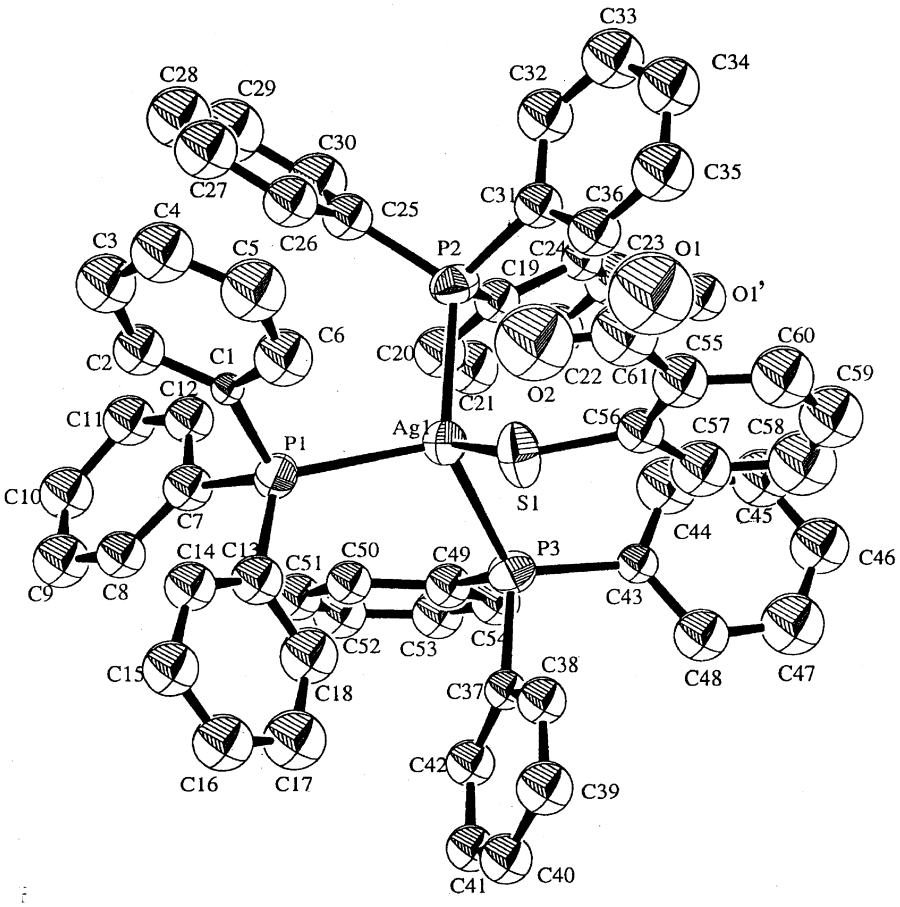


Fig. 2. Molecular structure of $[Ag(Htsa)(PPh_3)_3]$, **3**, with 50% probability ellipsoids.

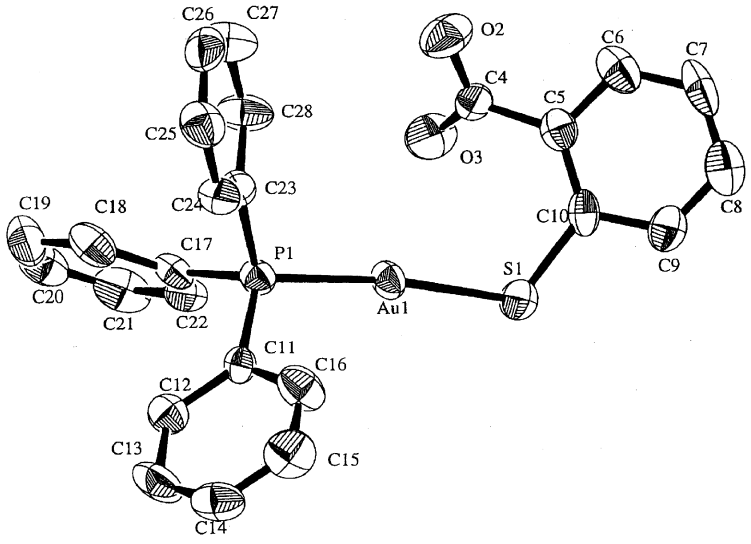


Fig. 3. Molecular structure of $[Au(Htsa)(PPh_3)]$, **4**, with 50% probability ellipsoids.

Table 2. Selected bond distances (Å) and angles (°) for the complexes

	3 [Ag(Htsa)(PPh_3)$_3$]				**4** [Au(Htsa)(PPh_3)]
Ag–S	2.608(7)	Ag–P2	2.577(6)	Au–S1	2.292(4)
Ag–P1	2.574(7)	Ag–P3	2.611(6)	Au–P1	2.260(3)
P1–C1	1.82(2)	P2–C19	1.83(2)	P1–C11	1.79(1)
P1–C7	1.84(2)	P2–C25	1.81(2)	P1–C17	1.79(1)
P1–C13	1.82(2)	P2–C31	1.81(2)	P1–C23	1.84(1)
S1–C56	1.76(2)	P3–C37	1.84(2)	S1–C10	1.77(1)
C55–C61	1.47(3)	P3–C43	1.85(2)	C5–C4	1.47(2)
C61–O1	1.17(4)	P3–C49	1.81(2)	C4–O2	1.30(1)
C61–O1′	1.40(6)			C4–O3	1.25(1)
C61–O2	1.28(3)				
(O1–O1′	0.75(6))				
S–Ag–P1	92.8(2)	S–Ag–P2	116.7(2)	S1–Au–P1	173.0(1)
Ag–P1–C1	114.2(6)	S–Ag–P3	108.7(2)	Au–P1–C11	111.3(4)
Ag–P1–C7	112.5(7)	P1–Ag–P2	112.0(2)	Au–P1–C17	113.7(4)
Ag–P1–C13	118.2(8)	P1–Ag–P3	112.9(2)	Au–P1–C23	114.0(4)
Ag–S–C56	117.4(7)	P2–Ag–P3	112.3(2)	Au–S1–C10	110.7(4)
S–C56–C55	123(1)	Ag–P2–C19	109.2(7)	S1–C10–C5	126.5(9)
C56–C55–C61	124(2)	Ag–P2–C25	119.1(7)	C10–C5–C4	125(1)
C55–C61–O1	129(3)	Ag–P2–C31	115.6(7)	C5–C4–O2	116(1)
C55–C61–O2	120(2)	Ag–P3–C37	116.7(7)	C5–C4–O3	122(1)
O1–C61–O2	110(3)	Ag–P3–C43	117.4(6)	O2–C4–O3	120(1)
		Ag–P3–C49	112.6(7)		

−90°C measured in CD_2Cl_2 of **3** showed two signals with equal intensity at 4.90 and 3.26 ppm, each with splittings, which are attributed to a coupling of ^{31}P with ^{109}Ag ($I = 1/2$) or ^{107}Ag ($I = 1/2$) nucleus as previously observed in [Ag(imd)(PPh_3)$_3$] [42], [AgCl(PPh_3)$_3$] [57], [Ag(dppe)$_2$]NO_3 (dppe = 1,2-bis(diphenylphosphino)ethane) [58], [Ag(pz)(PPh_3)$_3$] (Hpz = pyrazole) [59] and [Ag(triz)(PPh_3)$_2$]$_n$ (Htriz = 1,2,3- or 1,2,4-triazole) [43]. The coupling constants $^1J(^{109}Ag–^{31}P)$ and $^1J(^{107}Ag–^{31}P)$ were estimated as 285 and 266 Hz, respectively, and the chemical shift was as δ (^{31}P) = 4.08 ppm. These data are consistent with those of four-coordinate, tetrahedral complexes included in the above related complexes in solution [57–60].

The ^{31}P NMR spectrum of **3** at −90°C consisting of only two major peaks is in contrast to those of the related silver(I)–N bonding complexes such as [Ag(imd)(PPh_3)$_3$] [42], [Ag(pz)(PPh_3)$_3$] [59] and [Ag(triz)(PPh_3)$_2$]$_n$ [43], all of which have furthermore exhibited additional several signals due to various degrees of association in addition to dissociation of PPh_3 and perhaps also of the nitrogen-donor ligands, i.e. due to the dynamic exchange very rapidly in the NMR timescale. These results reveal that the four-coordinate geometry of **3** is kept in solution and the complex **3** is also present only as a monomeric species in solution. Thus, we conclude that the behavior of **3** in solution is unusually static.

^{109}Ag NMR spectra in $CDCl_3$ measured at 22°C exhibit only one resonance at 1196 ppm for **3a**, also suggesting that only a single species is present in solution, because of the monomeric structure of **3** kept in solution. The chemical shift is assignable to a four-coordinate silver(I) complex with sulfur and phosphorus donor atoms. This resonance is compared with those of the two-coordinate silver(I) complexes formed only by the bridged sulfur atom, previously measured at room temperature in D_2O; at 855.6 ppm for **1** [38] and at 868.7 ppm for {Na[Ag(Htma)] · 0.5H_2O)}$_n$ [36] (H_3tma = thiomalic acid; $HO_2CCH(SH)CH_2CO_2H$). Also, this chemical shift is compared with those of the averaged single peak due to the rapid, dynamic exchange among unequivalent ^{109}Ag species present in $CDCl_3$ solution at room temperature; at 1186 ppm for [Ag(imd)(PPh_3)$_3$] [42] and at 994 ppm for [Ag(1,2,3-triz)(PPh_3)$_2$]$_n$ and at 925 ppm for [Ag(1,2,4-triz)(PPh_3)$_2$]$_n$ [43].

In ^{1}H and ^{13}C NMR spectra measured in $CDCl_3$ at 22°C of the complexes **3**, **3a** and **4**, four proton and seven carbon resonances of the coordinating Htsa$^-$ ligand were completely assigned using several two-dimensional NMR (^{1}H–^{13}C COSY, ^{1}H–^{13}C HMBC and ^{1}H–^{13}C HMQC) methods and their chemical shifts are shown in Table 3.

4. CONCLUSIONS

In conclusion, the novel complex [Ag(Htsa)(PPh_3)$_3$], **3**, as a monomeric form of the oligomeric or polymeric silver(I) thiosalicylates **1** or **2** showing effective antimicrobial activities, has been isolated in good yield and also as its CH_2Cl_2 solvate, **3a**. These

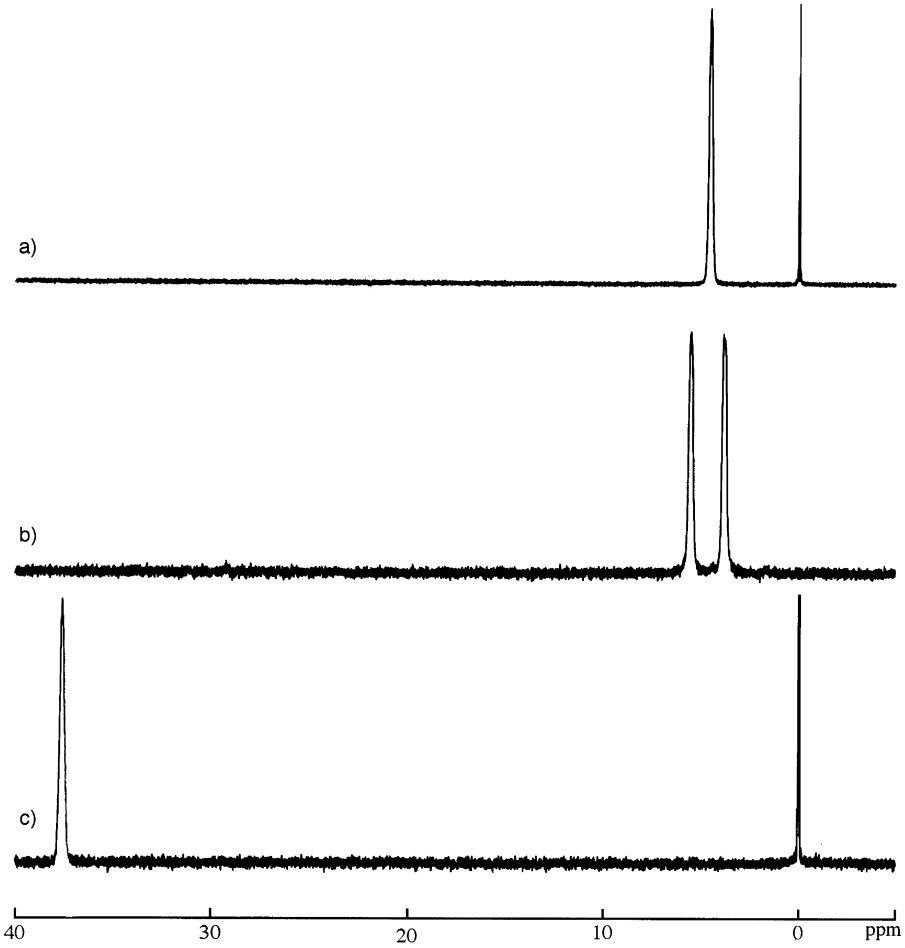
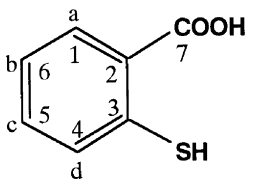


Fig. 4. $^{31}P\{^{1}H\}$ NMR spectra measured with reference to an external 25% H_3PO_4 of $[Ag(Htsa)(PPh_3)_3]$, **3**, measured (a) in $CDCl_3$ at 22°C and (b) in CD_2Cl_2 at −90°C and of (c) $[Au(Htsa)(PPh_3)]$, **4,** measured in $CDCl_3$ at 22°C.

Table 3. Assignment of ^{1}H and ^{13}C NMR signals of thiosalicylatometal(I) complexes[a]

^{1}H NMR								
		Ha			Hd	Hc	Hb	
$[Ag(Htsa)(PPh_3)_3]$	**3**	8.14			7.23[b]	6.62	6.82	
$[Ag(Htsa)(PPh_3)_3]\cdot CH_2Cl_2$	**3a**	8.15			7.19[b]	6.56	6.80	
$[Au(Htsa)(PPh_3)]$	**4**	8.33			7.73	7.30	7.21	
H_2tsa		8.04			7.63	7.35	7.57	
^{13}C NMR								
		C1	C2	C3	C4	C5	C6	C7
$[Ag(Htsa)(PPh_3)_3]$	**3**	132.44	130.10	149.19	136.85	130.58	122.20	170.01
$[Ag(Htsa)(PPh_3)_3]\cdot CH_2Cl_2$	**3a**	132.53	130.17	148.81	136.87	130.65	122.46	169.77
$[Au(Htsa)(PPh_3)]$	**4**	133.17	131.31	138.73	137.56	131.51	125.75	167.98
H_2tsa		128.11	138.93	133.23	125.00	131.54	125.97	167.59



H_2tsa : thiosalicylic acid

[a]Both ^{1}H and ^{13}C NMR spectra of **3**, **3a** and **4** were measured in $CDCl_3$ at 22°C with reference to an internal TMS and those of free ligand H_2tsa measured in DMSO-d_6. The assignment of the chemical shifts was based on the 2D-NMR (COSY, HMBC and HMQC) methods.

[b]These signals were overlapped with the PPh_3 multiplet signals.

complexes, **3** and **3a**, have been derived from three different ligand-exchange reactions. The interconversion relationship among three thiosalicylatosilver(I) complexes, **1**, **2** and **3** was clarified. The corresponding gold(I) analog, [Au(Htsa)(PPh_3)], **4**, was also isolated. From a synthetic viewpoint, the relative ordering of ligand replacement in the silver(I) complexes was found to be: Ag–P ≫ Ag–S > Ag–Cl > Ag–N, while that in the gold(I) complexes followed Au–P ≫ Au–S > Au–N > Au–Cl. The crystal structures of **3** and **4** were determined with single-crystal X-ray diffraction, suggesting the monomeric structure of **3** and the dimeric structure of **4** in the solid state. All complexes obtained have been fully characterized with complete elemental analyses, TG/DTA, FT-IR and multinuclear (^{1}H, ^{13}C, ^{31}P and ^{109}Ag) NMR spectroscopies. In particular, it was found that the monomeric, 4-coordinate geometry of **3** was kept in solution.

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