Two- and four-coordinated gold(I) complexes with aryldithiocarboxylates and triphenylphosphine. X-ray diffraction crystal structure of the $[Au(S_2CPh)PPh_3]$, $[Au(S_2CPh)(PPh_3)_2]$ and $[Au_{0.56}Cu_{0.44}(S_2C\text{-}p\text{-tolyl})(PPh_3)_2]$ complexes; NMR investigations of $[Au(S_2CAr)(PPh_3)_n]$ ($n=1$, 2) compounds in solution

Anna Maria Manotti Lanfredi*, Franco Ugozzoli
Istituto di Chimica Generale e Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, viale delle Scienze, 43100 Parma (Italy)

Fioretta Asaro, Giorgio Pellizer, Nazario Marsich and Annamaria Camus*
Dipartimento di Scienze Chimiche, via Valerio 38, 34127 Trieste (Italy)

(Received September 12, 1991; revised November 8, 1991)

Abstract

The synthesis of some Au(I) aryldithiocarboxylates (Ar = Ph, *o*-tolyl, *p*-tolyl) and their 1:1 and 1:2 complexes with triphenylphosphine are reported and their properties are compared with those of the corresponding Cu(I) and Ag(I) derivatives. Variable temperature ^1H and ^{13}C NMR solution spectra of the phosphino complexes are discussed and show a particularly strong metal–phosphine interaction in the $[Au(S_2CAr)PPh_3]$ molecules, which are fairly stable in solution. $[Au(S_2CAr)(PPh_3)_2]$ are stable in solution only below −30 °C. Approximate constants for the equilibria $[Au(S_2CAr)(PPh_3)_2] \rightleftharpoons [Au(S_2CAr)PPh_3] + PPh_3$ are reported. The intermolecular exchange of the phosphine between the mono and the bisphosphino complexes is fast and that between the latter and free phosphine even faster. Crystal and molecular structures have been determined by standard X-ray methods for the $[Au(S_2CPh)PPh_3]$ (**I**), $[Au(S_2CPh)(PPh_3)_2]$ (**II**) and $[(Au,Cu)S_2C\text{-}p\text{-tolyl}(PPh_3)_2]$ (**III**) complexes. In **I** there are two independent monomeric units in both of which the dithiobenzoate is monodentate, the metal atoms being coordinated by the ligands in a linear geometry. The gold atom in **II** and the cocrystallized copper/gold atoms in **III** are pseudo-tetrahedrally coordinated by the two PPh_3 and the chelating aryldithiocarboxylate anion. The four-membered chelate ring in **II** shows a remarkably long Au–S bond (2.859(4) Å). The coordination number of gold(I) and the strain involved in the formation of chelate rings with gold are discussed. Crystallographic data are as follows: $C_{25}H_{20}AuPS_2$ (**I**), monoclinic, space group $P2_1/n$, with $a = 19.952(4)$, $b = 12.733(4)$, $c = 19.894(4)$ Å, $\beta = 117.74(2)$ ° and $Z = 8$; $C_{43}H_{35}AuP_2S_2$ (**II**), monoclinic, space group $P2_1/n$, with $a = 20.712(3)$, $b = 19.552(2)$, $c = 9.180(2)$ Å, $\beta = 98.54(1)°$ and $Z = 4$; $C_{44}H_{37}Au_{0.56}Cu_{0.44}P_2S_2$ (**III**), orthorhombic, space group $P2_12_12_1$, with $a = 20.492(2)$, $b = 15.823(2)$, $c = 11.980(2)$ Å and $Z = 4$. The structures, solved by Patterson and Fourier methods, were refined by blocked full matrix least-squares to $R = 0.068$ (**I**), 0.044 (**II**) and 0.034 (**III**) for 3503 (**I**), 3242 (**II**) and 3273 (**III**) symmetry independent reflections.

Introduction

In recent years we have studied some aryl dithio- and perthiocarboxylates of copper(I) and silver(I) and their complexes with tertiary phosphine [1–7] and nitrogen containing ligands [8, 9]. Compounds of these kinds are becoming well known, the variety of the coordination modes of $ArCS_2$ and $ArCS_3$ ligands and the different behaviour with copper(I) and silver(I) [10] having stimulated the interest in such research. Information about the aryldithiocarboxylato complexes of gold(I) is much sparser and only $[Au(S_2C\text{-}o\text{-tolyl})]_6$ crystals have been structurally characterized [11] till now**. Taking also into account that a better knowledge of the gold(I) dithiolates and gold(I) phosphine complexes is important for their biological implications [13] we have undertaken an investigation of these compounds. In this paper we report the preparation of the $[Au(S_2CAr)]_n$, $[Au(S_2CAr)PPh_3]$ and $[Au(S_2CAr)(PPh_3)_2]$ compounds (Ar = Ph, *o*-T, *p*-T; T = tolyl), a comparative discussion of their solid state IR spectra,

---

*Authors to whom correspondence should be addressed.

**Another related interesting structure is that of an aliphatic dithiocarboxylate, the tetranuclear Au(I)dithioacetate [12].

X-ray diffraction studies of the molecular structures of [Au(S_2CPh)(PPh_3)] (**I**) and [Au(S_2CPh)(PPh_3)$_2$] (**II**) complexes, the isotropic NMR spectra and some results on the behaviour in solution of the phosphino derivatives. In addition the structure of a cocrystallized Au(I) and Cu(I) bis(triphenylphosphino)dithio-*p*-toluato complex (**III**) is discussed.

Experimental

Synthesis of the complexes

We report the preparations of the *p*-tolyldithiocarboxylato derivatives; the other compounds of the series were obtained by analogous procedures. Table 1 gives the analytical data and some characteristics of the products.

[AuS₂C-p-T]ₙ

2 ml of anhydrous CS_2 were added under nitrogen to 25 ml of an ethereal solution of Li-*p*-T 0.185 M (4.62 mmol), cooled to about −25 °C. The swift insertion reaction gave a red solution, whose temperature was allowed to rise to 0 °C. An ethereal solution of 0.60 g $HAuCl_4 \cdot nH_2O$ (1.50 mmol) was then slowly added, under stirring, immediately forming a plentiful precipitate from a dark-brown mother solution. After 2 h the suspension was filtered and the precipitate was washed three times with 20 ml each of a 1:1 water/methanol solution, then with methanol and then with ether till the washings became colourless. Yield practically quantitative, after drying under vacuum.

[Au(S₂C-p-T)PPh₃]

0.37 g (1.41 mmol) of PPh_3 was added to a suspension of 0.5 g (1.37 mmol) of [AuS_2C-*p*-T]$_n$ in 25 ml of toluene and the mixture was heated at reflux for 1 h. The powder formed was isolated by filtration and washed with Et_2O. It was then recrystallized from a mixture of CS_2 and petroleum ether (boiling range 30–50 °C).

[Au(S₂C-p-T)(PPh₃)₂]

0.182 g (0.50 mmol) of [AuS_2C-*p*-T]$_n$ was suspended in 20 ml of toluene and 0.65 g (2.50 mmol) of PPh_3 was added. The solid disappeared rapidly. After addition of the same volume of petroleum ether large crystals of a new product formed in a few minutes. Recrystallization from toluene or CS_2 and petroleum ether succeeds only if some PPh_3 is added to the solution.

[(Au,Cu)S₂C-p-T(PPh₃)₂]

This was obtained by treating a toluene suspension of a 1:1 mixture of Au(I) and Cu(I) *p*-tolyldithiocarboxylates with an excess of phosphine. The powder was precipitated by addition of petroleum ether from the green–brown solution and recrystallized from toluene

TABLE 1. Analytical data of the compounds

Compound	Colour	Melting point (°C)	Analysis (%)[a]			*MW* (wt./wt.%) (toluene)
			C	H	S	
[Au(S_2CPh)]$_n$[b]	deep brown	278 (dec)	23.8 (24.00)	1.6 (1.44)	17.9 (18.31)	
[Au(S_2CPh)PPh_3] (**I**)	red–violet	176–178	48.7 (49.02)	3.2 (3.29)	10.2 (10.47)	620(0.23) (612.5)
[Au(S_2CPh)(PPh_3)$_2$] (**II**)	brown	169–171	59.6 (59.04)	4.2 (4.03)	7.3 (7.33)	394(0.62) (874.7)
[Au(S_2C-*o*-T)]$_6$[c]	orange–red	226 (dec)	25.7 (26.38)	2.0 (1.94)	17.7 (17.60)	
[Au(S_2C-*o*-T)PPh_3]	light violet	170–172	50.0 (49.84)	3.4 (3.54)	10.1 (10.23)	615(0.70) (626.5)
[Au(S_2C-*o*-T)(PPh_3)$_2$]	orange[d]	152–153	60.0 (59.46)	4.2 (4.20)	7.1 (7.21)	412(1.05) (888.8)
[Au(S_2C-*p*-T)]$_n$	red–brown	280 (dec)	26.2 (26.38)	1.8 (1.94)	17.7 (17.60)	
[Au(S_2C-*p*-T)PPh_3]	deep violet	186–187	49.6 (49.84)	3.4 (3.54)	10.1 (10.23)	640(0.46) (626.5)
[Au(S_2C-*p*-T)(PPh_3)$_2$]	green–brown (dicroic)	148–150	59.6 (59.46)	4.2 (4.20)	7.3 (7.21)	430(0.78) (888.8)
[($Au_{0.56}Cu_{0.44}$)S_2C-*p*-T(PPh_3)$_2$] (**III**)	red–violet	146–148	62.5 (63.66)	4.3 (4.49)	7.9 (7.72) Cu 3.1 (3.37)	

---

[a] Calculated values in parentheses. [b] Lit. [11]. [c] Lit. [10]. [d] From toluene the dark-pink solvated complex [Au(S_2C-*o*-T)(PPh_3)$_2$]·½toluene is obtained; the compound loses the solvent at about 110 °C, turning to orange.

and petroleum ether in the presence of phosphine to give platelets, which appeared to be homogeneous under microscopic observation.

X-ray data collection and refinement

Crystal data and the most relevant parameters adopted in the X-ray data collection and refinement of compounds **I**, **II** and **III** are reported in Table 2.

The X-ray data collections were carried out at room temperature using graphite monochromatized Mo Kα radiation for compound **I** ($\lambda = 0.7107$ Å), Nb filtered Mo Kα radiation for compound **II** and Ni filtered Cu Kα radiation for compound **III** ($\lambda = 1.54178$ Å). The intensities were calculated from profile analysis following the method of Lehmann and Larsen [14] and corrected for Lorentz and polarization effects. Corrections for absorption effects were applied using the program ABSORB [15] at the end of the isotropic refinements. The absorption coefficients T as a function of the two polar angles ϕ and μ of the incident and diffracted beam paths are in the ranges: $1.413 \leqslant T \leqslant 0.810$ for **I**, $1.214 \leqslant T \leqslant 0.842$ for **II**, $1.092 \leqslant T \leqslant 0.905$ for **III**. The crystal lattice of compound **I**, which has been described by a monoclinic cell, seems also describable by an orthorhombic centered cell of parameters $a = 20.598$, $b = 34.108$, $c = 12.734$ Å (transformation matrix: $-1,0,-1/-1,-1,0/0,0,1$), but a simple test on the agreement between the intensities of symmetry equivalent reflections led us to exclude this possibility and to assume as the unit cell the monoclinic one. Three data collections performed on different crystals gave the same results.

The three structures were solved by Patterson and Fourier methods and refined using the SHELX package of crystallographic computer programs [16].

The structure of **I** was refined by a blocked full matrix least-squares method with 157 + 157 parameters. Parameters refined, for any cycle, were: the overall scale factor, positional parameters, anisotropic temperature factors for Au, S and P atoms. Isotropic temperature factors were assumed for C and H atoms. The atomic coordinates of H atoms were taken from their calculated positions with the geometrical constraint C–H = 1.0 Å and refined riding on the corresponding

TABLE 2. Experimental data for the X-ray diffraction studies

Compound	I	II	III
Formula	$C_{25}H_{20}AuPS_2$	$C_{43}H_{35}AuP_2S_2$	$C_{44}H_{37}Au_{0.56}Cu_{0.44}P_2S_2$
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
Cell dimensions (a)			
a (Å)	19.952(4)	20.712(3)	20.492(2)
b (Å)	12.733(4)	19.552(2)	15.823(2)
c (Å)	19.894(4)	9.180(2)	11.980(2)
α (°)	90	90	90
β (°)	117.74(2)	98.54(1)	90
γ (°)	90	90	90
ν (Å^3)	4473(2)	3676(1)	3884(1)
Z	8	4	4
D_{calc}(Mg m^{-3})	1.819	1.581	1.419
Molecular weight	612.49	874.78	830.11
Crystal dimensions (mm)	0.3×0.2×0.2	0.2×0.4×0.2	0.1×0.2×0.3
Linear absorption coefficient (cm^{-1})	68.25	42.18	63.86
Diffractometer	Philips PW1100	Siemens AED	Siemens AED
Scan type	ω–2θ	θ–2θ	θ–2θ
Scan speed	3–12 deg/min	3–12 deg/min	3–12 deg/min
Scan width (°)	b	b	b
Radiation	Mo Kα	Mo Kα	Cu Kα
2θ range (°)	6–46	5–50	6–140
Reflections measured	$\pm h, \pm k, l$	$\pm h, k, l$	h, k, l
Total data measured	12909	7674	4148
Criterion for observations	$I \geqslant 2\sigma(I)$	$I \geqslant 3\sigma(I)$	$I \geqslant 3\sigma(I)$
Observed data measured	6538	3512	3273
Unique observed data	3503	3242	3273
Agreement between equivalent observed reflections	0.036	0.033	0.0
No. variables	314	468	481
$F(000)$	2368	1736	1680
Final R	0.068	0.044	0.034
Final R_w	0.054	0.044	0.030

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 25–30 carefully centered reflections chosen from diverse regions of reciprocal spaces. [b] $(\theta - 0.65) - [\theta + (0.65 + \Delta\theta)]$; $\Delta\theta = [(\lambda_{\alpha_1} - \lambda_{\alpha_2})/\lambda] \tan \theta$.

carbon atoms. The refinement was stopped at $R=0.068$, $R_w=0.054$, $w=(\sigma(F_o))^{-2}$.

The structures of **II** and **III** were refined by full matrix least-squares methods with a total of 468 and 481 parameters, respectively. Parameters refined were: the overall scale factor, positional parameters and anisotropic temperature factors for all the non-hydrogen atoms; for the H atoms, whose atomic coordinates were calculated and refined as for compound **I**, isotropic temperature factors were assumed for both **II** and **III**. The occupancy factors of the Au and Cu atoms were also refined for **III**. The refinements were stopped at $R=0.044$ (unit weights) for **II** and $R=0.034$, $R_w=0.030$ with $w=(\sigma(F_o))^{-2}$ for **III**.

Since an enantiomorphic crystal can be built up from the achiral molecule **III**, which crystallizes in the $P2_12_12_1$ space group, an attempted refinement with the $-x,-y,-z$ atomic coordinates was carried out. The refinement converged at $R=0.059$ so that the latter case was excluded. Atomic scattering factors were obtained by analytical approximation (see ref. 17).

The calculations were performed on the GOULD POWERNODE 6040 of Centro di Studio per la Strutturistica Diffrattometrica CNR (Parma) and on the CRAY Y-MP8/432 computer of the 'Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale' (CINECA, Casalecchio, Bologna). The geometrical calculations were obtained by PARST [18] and the drawings were obtained by PLUTO78 [19].

Final atomic coordinates for the non hydrogen atoms of **I**, **II** and **III** are given in Tables 3, 4 and 5, respectively.

Bibliographic searches were obtained from the Cambridge Crystallographic Data Bank through Servizio italiano per la diffusione dei dati cristallografici, Parma [20].

IR spectra

IR spectra were run on a Perkin-Elmer 983 G spectrophotometer, as Nujol mulls or KBr pellets.

NMR spectra

NMR spectra were recorded with a Bruker WP 80 spectrometer equipped with an Aspect 2000 computer. For ^{13}C spectra the samples were $CDCl_3$ solutions of the complexes in 10 mm tubes, TMS was used as internal standard, spectral width was 6000 Hz, digital resolution 0.75 Hz/pt, flip angle 30°; ^1H broad band decoupling was used. Assignment of quaternary carbons was confirmed through the Bruker QUATD.AU pulse sequence. For ^{31}P spectra the samples were dissolved either in $CDCl_3$ or CD_2Cl_2 or a CD_2Cl_2/toluene 3:1 mixture, in 10 mm tubes; the chemical shifts were referenced to the resonance frequency of a sample of free phosphine in the same solvent and at the same

TABLE 3. Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of **I**

Atom	*x/a*	*y/b*	*z/c*
Au(1)	2514(1)	5798(1)	6625(1)
S(11)	3007(3)	5958(5)	7921(2)
S(21)	2144(4)	3939(6)	7633(4)
P(11)	2049(4)	5633(5)	5350(3)
Au(2)	6702(1)	4069(1)	7696(1)
S(12)	8024(2)	3989(5)	8278(3)
S(22)	7659(4)	5896(5)	7336(3)
P(12)	5427(3)	4230(6)	7148(3)
C(11)	2763(9)	4811(9)	8223(6)
C(21)	3071(13)	4713(17)	9018(7)
C(31)	3799(15)	5023(19)	9511(15)
C(41)	4112(16)	4830(17)	10326(15)
C(51)	3659(12)	4422(16)	10652(14)
C(61)	2895(14)	4141(20)	10124(13)
C(71)	2632(12)	4232(18)	9323(12)
C(91)	2545(12)	6357(15)	4941(13)
C(101)	3254(14)	6749(18)	5367(17)
C(111)	3626(17)	7301(19)	5046(16)
C(121)	3271(16)	7460(20)	4260(16)
C(131)	2497(17)	7161(21)	3770(20)
C(141)	2160(16)	6574(18)	4147(15)
C(151)	2208(11)	4280(18)	5162(12)
C(161)	2194(15)	3443(20)	5594(19)
C(171)	2256(13)	2403(22)	5483(15)
C(181)	2325(12)	2174(21)	4857(13)
C(191)	2353(12)	2973(19)	4405(15)
C(201)	2267(11)	3951(19)	4550(13)
C(211)	1026(12)	5957(19)	4865(11)
C(221)	486(15)	5210(23)	4362(14)
C(231)	−261(15)	5539(19)	3975(14)
C(241)	−486(16)	6507(19)	4057(14)
C(251)	56(13)	7267(19)	4531(12)
C(261)	830(15)	6986(20)	4931(14)
C(12)	8304(6)	5072(9)	7911(9)
C(22)	9093(6)	5145(16)	8188(13)
C(32)	9293(14)	5541(17)	7672(15)
C(42)	10112(13)	5640(18)	7897(15)
C(52)	10605(16)	5296(17)	8620(14)
C(62)	10398(14)	4941(17)	9153(16)
C(72)	9585(15)	4816(19)	8912(16)
C(92)	5250(11)	5614(14)	7247(10)
C(102)	5636(14)	6426(17)	7184(12)
C(112)	5512(13)	7446(19)	7261(11)
C(122)	4901(12)	7707(20)	7357(12)
C(132)	4467(16)	6962(20)	7443(13)
C(142)	4636(13)	5900(22)	7350(11)
C(152)	4968(12)	3516(15)	7551(12)
C(162)	4169(13)	3248(16)	7121(15)
C(172)	3789(20)	2712(21)	7485(18)
C(182)	4229(15)	2543(18)	8289(16)
C(192)	5009(15)	2717(18)	8664(16)
C(202)	5376(15)	3168(16)	8284(14)
C(212)	4971(10)	3952(14)	6157(10)
C(222)	5018(14)	2991(19)	5871(15)
C(232)	4597(12)	2674(19)	5151(13)
C(242)	4162(14)	3375(19)	4666(16)
C(252)	4122(18)	4502(28)	4933(21)
C(262)	4518(13)	4707(21)	5675(14)

TABLE 4. Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of **II**

Atom	x/a	y/b	z/c
Au	359(1)	2102(1)	1457(1)
P(1)	1175(2)	1323(2)	1184(4)
P(2)	149(2)	3248(2)	901(4)
S(1)	−336(2)	1721(2)	3479(5)
S(2)	−891(2)	1530(3)	380(5)
C(1)	−972(8)	1632(9)	2185(16)
C(2)	−1652(8)	1589(9)	2580(19)
C(3)	−2157(9)	1255(13)	1734(23)
C(4)	−2769(11)	1241(17)	2098(28)
C(5)	−2904(10)	1538(16)	3324(27)
C(6)	−2415(9)	1911(10)	4207(24)
C(7)	−1787(9)	1924(11)	3822(20)
C(9)	1222(7)	1113(9)	−738(16)
C(10)	1269(9)	490(10)	−1255(20)
C(11)	1298(10)	366(18)	−2763(23)
C(12)	1272(11)	914(13)	−3676(22)
C(13)	1221(12)	1547(12)	−3183(20)
C(14)	1197(9)	1670(9)	−1721(19)
C(15)	1995(8)	1618(14)	1893(21)
C(16)	2536(8)	1485(11)	1255(21)
C(17)	3141(10)	1735(11)	1886(26)
C(18)	3205(9)	2102(13)	3117(26)
C(19)	2674(10)	2261(14)	3779(24)
C(20)	2079(10)	2024(11)	3174(22)
C(21)	1132(8)	498(10)	2079(18)
C(22)	517(10)	194(12)	2037(22)
C(23)	457(11)	−413(11)	2736(24)
C(24)	1015(11)	−752(10)	3438(22)
C(25)	1609(11)	−475(11)	3497(22)
C(26)	1679(9)	164(9)	2811(19)
C(27)	755(8)	3834(9)	1920(17)
C(28)	1413(9)	3612(13)	2130(21)
C(29)	1904(13)	4012(15)	2893(26)
C(30)	1721(11)	4630(12)	3479(22)
C(31)	1082(11)	4828(11)	3294(21)
C(32)	602(10)	4432(9)	2517(19)
C(33)	207(7)	3416(8)	−1027(16)
C(34)	457(8)	4052(11)	−1491(20)
C(35)	496(10)	4168(16)	−2947(22)
C(36)	270(11)	3633(12)	−3978(22)
C(37)	24(10)	3062(15)	−3524(20)
C(38)	−4(8)	2932(14)	−2054(16)
C(39)	−624(8)	3642(8)	1188(18)
C(40)	−927(9)	4156(11)	243(22)
C(41)	−1503(9)	4430(12)	480(23)
C(42)	−1807(11)	4232(15)	1661(28)
C(43)	−1511(11)	3729(13)	2570(26)
C(44)	−933(10)	3443(12)	2307(21)

TABLE 5. Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of **III**[a]

Atom	x/a	y/b	z/c
M	7301(1)	2568(1)	5938(1)
S(1)	8529(1)	3135(1)	6161(2)
S(2)	7957(1)	1928(1)	7729(2)
P(1)	6430(1)	3476(1)	6488(2)
P(2)	7358(1)	1550(1)	4451(2)
C(1)	8591(3)	2482(5)	7270(6)
C(2)	9239(4)	2404(5)	7832(6)
C(3)	9812(4)	2647(6)	7288(8)
C(4)	10421(4)	2559(7)	7820(7)
C(5)	10479(4)	2239(5)	8889(8)
C(6)	9905(4)	2001(5)	9429(9)
C(7)	9286(4)	2077(5)	8895(7)
C(8)	11156(4)	2114(6)	9423(9)
C(9)	6147(4)	4220(5)	5446(7)
C(10)	6044(4)	5070(5)	5596(8)
C(11)	5846(4)	5596(6)	4761(9)
C(12)	5733(5)	5293(6)	3706(10)
C(13)	5831(5)	4425(6)	3516(10)
C(14)	6047(4)	3901(5)	4371(7)
C(15)	5689(4)	2920(5)	6860(7)
C(16)	5074(5)	3166(7)	6583(9)
C(17)	4529(5)	2692(8)	6899(11)
C(18)	4595(5)	1967(7)	7457(10)
C(19)	5205(5)	1700(6)	7756(9)
C(20)	5761(5)	2177(5)	7476(7)
C(21)	6612(4)	4130(5)	7704(7)
C(22)	7234(4)	4211(5)	8023(7)
C(23)	7408(5)	4693(5)	8940(8)
C(24)	6930(4)	5094(6)	9541(9)
C(25)	6290(5)	5028(6)	9250(9)
C(26)	6137(4)	4532(6)	8308(8)
C(27)	6591(4)	1010(5)	4195(8)
C(28)	6154(5)	980(8)	5060(11)
C(29)	5536(6)	591(9)	4948(12)
C(30)	5367(5)	187(7)	4017(11)
C(31)	5794(5)	207(7)	3189(10)
C(32)	6428(5)	618(6)	3224(9)
C(33)	7590(4)	1995(5)	3106(7)
C(34)	7818(4)	1488(6)	2235(8)
C(35)	7975(5)	1858(7)	1221(9)
C(36)	7925(5)	2714(8)	1076(10)
C(37)	7727(5)	3239(6)	1961(9)
C(38)	7560(5)	2875(5)	2976(9)
C(39)	7952(4)	697(5)	4628(7)
C(40)	7797(4)	−157(5)	4449(8)
C(41)	8251(4)	−766(6)	4648(9)
C(42)	8886(5)	−531(6)	4979(8)
C(43)	9038(5)	299(6)	5146(9)
C(44)	8559(4)	927(6)	4989(8)

[a]In **III** metal site M was 56% Au and 0.44% Cu.

temperature, spectral width was 6000 Hz, digital resolution 1.5 Hz/pt, flip angle 30°; ^1H broad band decoupling was used. For ^1H spectra the samples were dissolved either in $CDCl_3$ or C_6D_6, in 5 mm tubes, spectral width was 1000 Hz, digital resolution 0.125 Hz/pt, flip angle 30°. Assignment of some resonances was confirmed by selective homonuclear decoupling.

Results and discussion

The Cu(I) and Ag(I) perthiocarboxylates we prepared [2,5,6] were obtained following the procedure of Fackler *et al.* [21], by treating aqueous solutions of $CuCl_2 \cdot 3H_2O$ or $AgNO_3$ with the reagent formed from the corresponding aldehyde and ammonium polysulfide, in basic media. The same reagent mixture gave only the dithiocarboxylates with $HAuCl_4 \cdot nH_2O$, nor could the perthio derivatives be formed by addition of sulfur in refluxing toluene, as for the other coinage metals.

The dithiocarboxylates are however more conveniently prepared by reaction with $ArCS_2Li$ as reported in 'Experimental'. Like the copper and silver derivatives, these compounds are deeply coloured. Their solubility is very poor, even in boiling pyridine and only the *ortho* derivative is sufficiently soluble in CS_2 to be recrystallized and spectroscopically investigated [11].

More soluble, as usual, are the complexes of the Au(I) dithiocarboxylates with triphenylphosphine ($o-T>p-T>Ph$). A series of mono- and bis-triphenylphosphino complexes could be prepared, but the latter could be isolated only in the presence of a large excess of triphenylphosphine. They undergo extensive dissociation in solution with loss of a PPh_3 molecule, as indicated by the low values of the molecular weights measured in toluene and dichloroethane at 44 °C (Table 1) and by the NMR spectra (see below). Unlike the corresponding silver compounds [6, 7], the monophosphino complexes are mononuclear, as confirmed by the X-ray diffraction study of the $[Au(S_2CPh)PPh_3]$ compound. Curiously, the colours of the gold monophosphino dithiocarboxylates correspond to those of the silver bisphosphino complexes and vice versa.

Compound **I** is described by the two crystallographically independent although similar molecules. Views of them and of complexes **II** and **III** are shown in Figs. 1–3 respectively. Selected bond distances and angles are given in Table 6 for **I** and in Table 7 for both **II** and **III** complexes.

In the two monomeric species present in **I**, the metal is linearly coordinated by the P atom from a triphenylphosphine molecule and one sulfur atom from a dithiobenzoato ligand. The bond angles subtended at the Au(1) and Au(2) atoms are 179.0(3) and 177.2(3)°, respectively. Unlike the bridging and/or chelating behaviour of the dithioarylato ligands observed in other Cu(I) and Ag(I) complexes [1, 3, 5, 8], in compound **I** the dithiobenzoates act as monodentate ligands, while the S(21) and S(22) atoms are involved in weak intramolecular contacts with the metal (Au(1)...S(21) = 3.398(9) and Au(2)...S(22) = 3.293(8) Å]. The strongest of these interactions is responsible for the slight bending ($\approx 3°$) from ideal linearity of the P(12)–Au(2)–S(12) angle, as observed in the related $[Au\{S_2CN(C_2H_5)_2\}PPh_3]$ dithiocarbamate complex [22], whereas the weakest Au–S interaction does not substantially affect the linearity of the P(11)–Au(1)–S(11) system (179.0(3)°). The Au(1)–P(11), Au(2)–P(12) and Au(2)–S(12) bond lengths agree well with the corresponding distances in the cited dithiocarbamate complex [22], but the distance between the Au(I) and S(11) atoms is significantly shorter (2.301(4) versus 2.338(3) Å).

The C–S distances of the dithiocarboxylato moieties are significantly different from each other in both monomeric species and show some localization of the

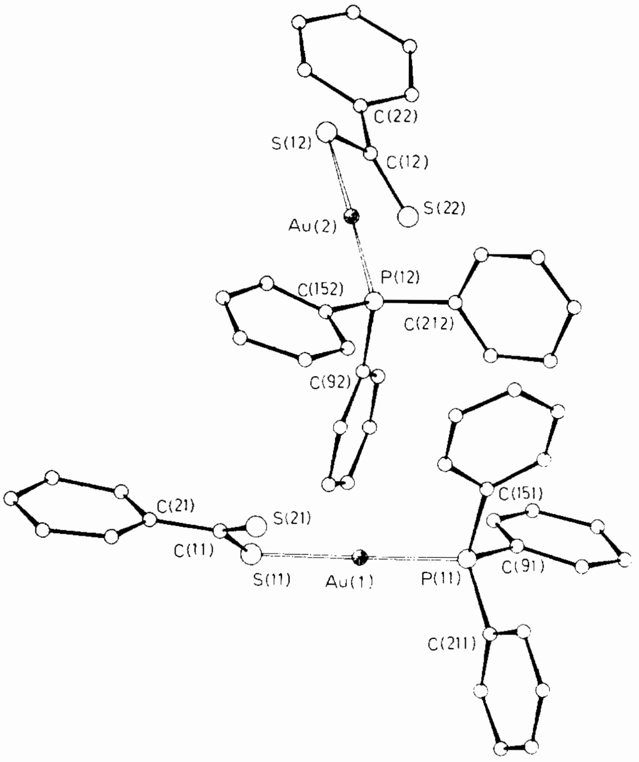


Fig. 1. Perspective view of the two independent molecules in $[Au(S_2CPh)PPh_3]$ (**I**) with the atomic numbering scheme.

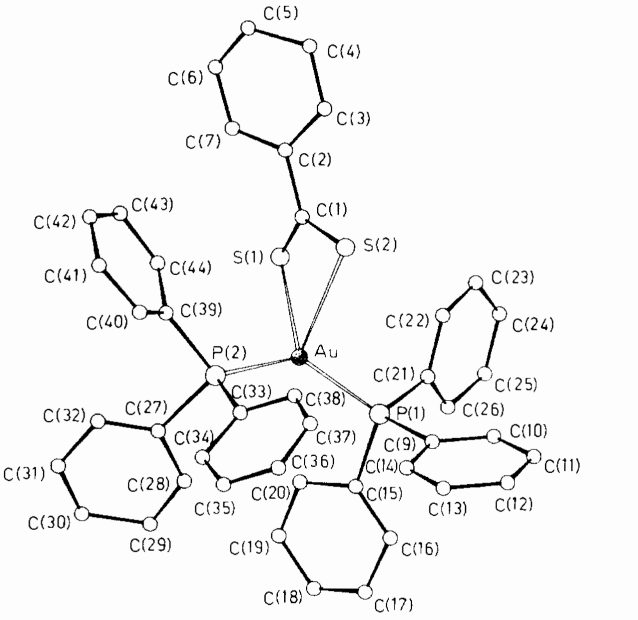


Fig. 2. Perspective view of the complex $[Au(S_2CPh)(PPh_3)_2]$ (**II**) with the labelling scheme.

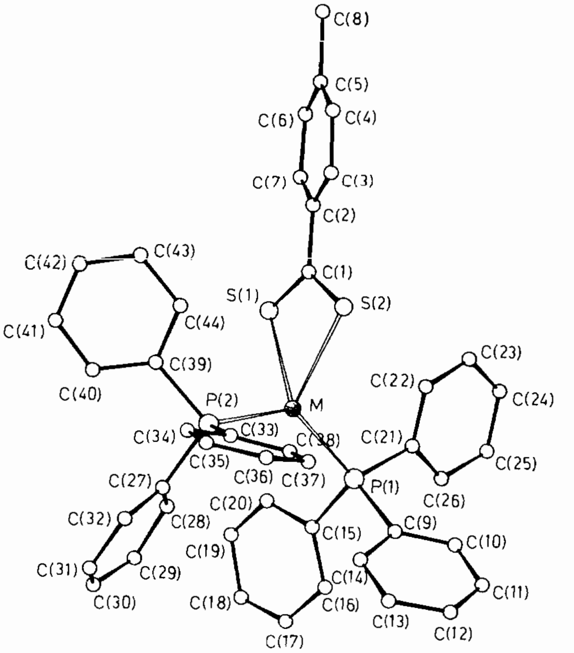


Fig. 3. Perspective view of the complex [M(S_2C-*p*-tolyl)(PPh_3)$_2$] (M = Au,Cu) (**III**) with the labelling scheme. Metal site M was 56% Au and 44% Cu.

double bond character in the C–S bonds to the uncoordinated sulphur atoms, like in the [Au{$S_2CN(C_2H_5)_2$}PPh_3] complex. The Au(1) and Au(2) atoms are 0.434(2) and 0.151(2) Å out the plane passing through the C(11)S(11)S(21) and C(12)S(12)S(22) groups, which are tilted from the associated aryl groups by 37.2(6) and 34.6(5)°, respectively.

The Au...Au contacts, involving gold(I) atoms from monomeric species related by the glide symmetry plane are in the range 7.269(3)–7.321(3) Å; the shortest distance between metal atoms of the two crystallographically independent complexes is 7.914(3) Å, with an angle, between the weighted least-squares lines associated to the P–Au–S systems, of 109.4(2)°.

Interesting is the different packing mode determined by the action of the symmetry centers on the two independent molecules of complex **I**. In fact, while the packing of the Au(2) complexes is determined by normal van der Waals contacts, the Au(1) monomeric species are associated in dimers by intermolecular H...S contacts between phenyl ring H atoms and uncoordinated sulfur atoms (H(241)...S(21) $(-x,1-y,1-z)=2.76(2)$ Å; C(241)–H(241)–S(21)$(-x,1-y,1-z)=131(2)$°) fulfilling the geometrical requirements for hydrogen bonds. The Au(1)...Au(1) separation in the dimers is 9.428(4) Å.

The complexes [Au(S_2CPh)(PPh_3)$_2$] and [(Au,Cu)S_2C-*p*-T(PPh_3)$_2$] are mononuclear in the solid state. The arrangements around the gold atom in **II** and gold/copper cocrystallized atoms in **III** are quite similar: two phosphorus atoms from monodentate PPh_3 ligands and two sulfur atoms from the chelating dithiocarboxylato ligands are pseudo-tetrahedrally coordinated to the central metals. A systematic search of the Cambridge Crystallographic Data File has shown

TABLE 6. Relevant bond distances (Å) and angles (°) in [Au(S_2CPh)PPh_3] (**I**)

Molecule 1		Molecule2	
Au(1)–S(11)	2.301(4)	Au(2)–S(12)	2.338(4)
Au(1)–P(11)	2.269(6)	Au(2)–P(12)	2.263(6)
C(11)–S(11)	1.73(2)	C(12)–S(12)	1.77(2)
C(11)–S(21)	1.67(1)	C(12)–S(22)	1.64(1)
C(11)–C(21)	1.41(2)	C(12)–C(22)	1.41(2)
C(21)–C(31)	1.38(3)	C(22)–C(32)	1.36(4)
C(31)–C(41)	1.46(4)	C(32)–C(42)	1.48(4)
C(41)–C(51)	1.43(5)	C(42)–C(52)	1.38(3)
C(51)–C(61)	1.44(3)	C(52)–C(62)	1.38(5)
C(21)–C(71)	1.42(4)	C(22)–C(72)	1.38(3)
P(11)–C(91)	1.80(3)	P(12)–C(92)	1.83(2)
P(11)–C(151)	1.82(2)	P(12)–C(152)	1.73(3)
P(11)–C(211)	1.85(2)	P(12)–C(212)	1.78(2)
P(11)–Au(1)–S(11)	179.0(3)	P(12)–Au(2)–S(12)	177.2(3)
Au(1)–S(11)–C(11)	105.7(4)	Au(2)–S(12)–C(12)	105.2(5)
S(11)–C(11)–S(21)	123.5(7)	S(12)–C(12)–S(22)	119.4(9)
S(11)–C(11)–C(21)	114.7(10)	S(22)–C(12)–C(22)	113.6(12)
S(21)–C(11)–C(21)	121.5(12)	S(22)–C(12)–C(22)	127.0(12)
Au(1)–P(11)–C(91)	117.8(8)	Au(2)–P(12)–C(92)	105.4(7)
Au(1)–P(11)–C(151)	107.3(7)	Au(2)–P(12)–C(152)	116.6(8)
Au(1)–P(11)–C(211)	109.9(8)	Au(2)–P(12)–C(212)	113.3(7)
C(91)–P(11)–C(151)	101.9(11)	C(92)–P(12)–C(152)	106.7(11)
C(91)–P(11)–C(211)	110.8(10)	C(92)–P(12)–C(212)	106.7(9)
C(151)–P(11)–C(211)	111.0(11)	C(152)–P(12)–C(212)	107.5(10)

TABLE 7. Relevant bond distances (Å) and angles (°) in $[Au(S_2CPh)(PPh_3)_2]$ (**II**) and $[(Au,Cu)(S_2C\text{-}p\text{-tolyl})(PPh_3)_2]$ (**III**)

	Compound		
	II (M = Au)	**III**[a] (M = Au,Cu)	**IV**[b] (M = Cu)
M–S(1)	2.620(5)	2.685(3)	2.423(2)
M–S(2)	2.859(4)	2.727(3)	2.418(2)
M–P(1)	2.316(4)	2.384(3)	2.258(2)
M–P(2)	2.325(4)	2.405(3)	2.254(1)
S(1)–C(1)	1.65(2)	1.688(8)	1.698(4)
S(2)–C(1)	1.70(2)	1.661(7)	1.689(4)
P(1)–C(9)	1.83(2)	1.811(8)	1.830(4)
P(1)–C(15)	1.82(2)	1.811(8)	1.826(5)
P(1)–C(21)	1.82(2)	1.825(9)	1.819(4)
P(2)–C(27)	1.85(2)	1.815(8)	1.829(4)
P(2)–C(33)	1.82(2)	1.822(9)	1.826(4)
P(2)–C(39)	1.83(2)	1.830(8)	1.822(5)
C(1)–C(2)	1.51(2)	1.494(10)	1.479(5)
C(2)–C(3)	1.37(3)	1.397(12)	1.396(6)
C(2)–C(7)	1.38(3)	1.378(11)	1.398(6)
C(3)–C(4)	1.36(3)	1.408(12)	1.379(6)
C(4)–C(5)	1.33(4)	1.382(13)	1.377(7)
C(5)–C(6)	1.40(3)	1.394(12)	1.390(8)
C(6)–C(7)	1.40(3)	1.426(12)	1.381(7)
C(5)–C(8)		1.540(12)	1.508(9)
P(1)–M–P(2)	136.5(1)	130.2(1)	124.2(1)
S(2)–M–P(2)	99.8(1)	108.1(1)	108.9(1)
S(2)–M–P(1)	110.1(2)	112.1(1)	113.5(1)
S(1)–M–P(2)	109.0(1)	104.6(1)	119.0(1)
S(1)–M–P(1)	112.1(1)	118.2(1)	106.6(1)
S(1)–M–S(2)	64.5(1)	65.4(1)	73.9(1)
C(1)–S(1)–M	89.1(5)	86.8(2)	83.6(2)
C(1)–S(2)–M	80.4(6)	85.9(3)	83.9(2)
C(21)–P(1)–M	116.7(6)	114.2(3)	118.6(2)
C(15)–P(1)–M	114.2(8)	113.8(3)	111.0(2)
C(9)–P(1)–M	113.4(5)	116.2(3)	115.2(2)
C(15)–P(1)–C(21)	103.0(8)	104.5(4)	103.2(2)
C(9)–P(1)–C(21)	104.5(8)	104.3(4)	102.0(2)
C(9)–P(1)–C(15)	103.6(7)	102.5(4)	105.5(2)
C(39)–P(2)–M	120.9(5)	116.1(3)	115.1(2)
C(33)–P(2)–M	110.5(5)	114.2(3)	112.0(2)
C(27)–P(2)–M	113.3(5)	113.5(3)	118.3(2)
C(33)–P(2)–C(39)	104.4(7)	102.4(4)	103.6(2)
C(27)–P(2)–C(39)	102.1(8)	104.4(4)	103.5(2)
C(27)–P(2)–C(33)	104.0(7)	105.0(4)	102.5(2)
S(1)–C(1)–S(2)	122.1(10)	121.7(4)	118.4(3)
S(2)–C(1)–C(2)	117.3(11)	120.2(6)	121.0(3)
S(1)–C(1)–C(2)	120.5(11)	118.2(6)	120.6(3)

[a] For **II** metal site M was 56.0% Au and 44.0% Cu. [b] Ref. 5.

that structures of gold monomers with chelating dithiocarboxylato ligands were till now known for gold(III) [23] but not for gold(I) complexes.

The analysis of the electron density difference map of the mixed compound **III** shows no residual peaks close to the positions of the metal bonded sulfur and phosphorous atoms. This suggests that those sites are uniformly singly occupied and not occupied by a weighed combination of the corresponding atoms, one bonded to Au and the other to Cu atoms. So **III** can be considered, together with a (Cu(I),Ag(I)) perthioarylate we previously synthesized [6], one of the few examples of crystals containing two different coinage metals and having structural uniformity [24].

The structures of **II** and **III**, whose crystals are monoclinic and orthorhombic, respectively, are very similar to that of the $[Cu(S_2C\text{-}p\text{-}T)(PPh_3)_2]$ complex (**IV**) [5], which crystallizes, together with PPh_3S molecules interposed in the lattice, in the triclinic $P\bar{1}$ space group. There are, however, some differences in the coordination distances and the geometry of the CS_2 groups. The values found for the metal–donor atom bonds of the cocrystallized complex **III**, are not always the average of those of the pure compounds, as could be expected. For example the M–P distances in **III** are appreciably longer than the corresponding bond lengths in complexes **II** and **IV** (2.384(3)–2.405(3) Å (**III**) versus 2.316(4)–2.325(4) (**II**) and 2.258(2)–2.254(1) (**IV**) Å) and also some corresponding bond angles deviate from the expected trend.

In the pure gold(I) complex a remarkable difference between the two Au–S distances in the chelate ring (2.859(4) versus 2.620(5) Å) is observed. The shorter one lies adjacent to the C–S bond which shows some localization of double bond character. In **III** the (Au,Cu)–S distances are significantly different (2.727(3) versus 2.685(3) Å) and the CS_2 group is less asymmetrically chelating than in **II**. In **IV** the Cu–S bond lengths are similar (2.423(2) and 2.418(2) Å) indicating that the dithioarylato group acts as a symmetrically chelating ligand. In complexes **III** and **IV** the C–S distances are consistent with delocalization of the double bond in the CS_2 moiety. This fragment, which only for the above compounds is roughly coplanar with the metal centre (the displacement of the metal atom from the plane through the relative CS_2 portion is 0.934(3), 0.209(2) and 0.055(2) Å in **II**, **III** and **IV**, respectively), is tilted with respect to the associated aryl group by 26.6(7)° in **II**, 8.9(4)° in **III** and 5.4(2)° in **IV**.

The factors, which determine the above-mentioned features, are not clear but seems associated with the strain involved in the formation of chelate rings by this type of ligand, higher for gold(I) than for copper(I) or gold(III). By comparison with the $[Au(dtc)(S_2C_4N_2]$ gold(III) complex [25], where symmetrically bonded chelating dithiocarbamato ligands are present (Au–S = 2.324(5)–2.329(5) Å), the relevant weakening in **II** of an Au–S bond of the chelate ring (2.859(4) versus 2.620(5) Å) could explain its opening to give complexes with lower coordination numbers. Gold(I) gives frequently linear two-coordinated complexes, while three- and four-coordinated species are less common, in particular four coordination and chelation. The few other structurally characterized four-coordinated monomeric complexes of gold(I), featuring a pseudo-tetrahedral P_3S donor set [26, 27], also contain unusually long Au–S distances, e.g. 2.787(4) Å in $[AuSCN(PPh_3)_3]$ [26] and 2.791(3) Å in the monoclinic form of the compound $[AuSCN(PPh_3)_3]\cdot H_2O$ [27]. The distances are correlated with steric crowding about the metal atoms. Moreover, it is noteworthy that in tetrahedral gold(I) complexes with chelating phosphino ligands such as the cationic $[Au(diphos)_2]^+$, the chelate ring opening is expected to be a critical step in antitumour activity [28, 29].

Though the metal in our complex **II** has been recognized as tetra-coordinated, the Au–P distances (2.316(4)–2.325(4) Å) are more similar to those found in the trigonal planar $[AuSCN(PPh_3)_2]$ complex (2.346(4)–2.349(4) Å) [30] than to the Au–P bond lengths in the other known tetrahedral triphosphino complexes [26, 27], ranging from 2.384(3) to 2.413(3) Å. Also the displacement of the metal from the least-squares plane through the P(1), P(2) and S(1) atoms is 0.210(1) Å, in good agreement with the value (0.2 Å) in the ionic trigonal planar moiety of the $[Au\{P(C_6H_5)_3\}_3][B_9H_{12}S]$ compound [31].

The Au/Cu–P distances in **III** (2.384(3)–2.405(3) Å), longer than those of the corresponding pure gold complex **II** and similar to the Au–P bond lengths found in the cited triphosphino tetrahedral complexes [26, 27], are probably due to the presence of copper(I) promoting tetrahedral arrangement of the cocrystallized atoms and to packing forces different from those present in complex **II**.

Even if complexes **II**, **III** and **IV** show the same configuration, they do not form an isomorphous series of crystals, as observed for the silver, cocrystallized copper/silver and copper tetrameric perthio-*o*-tolylcarboxylato complexes [6]. The steric requirements of the dithiobenzoato and dithio-*p*-toluato ligands and the presence of triphenylphosphine sulfide molecules in **IV** play a relevant role in precluding the formation of such an isomorphous series.

IR spectra

We dispose now, for the coinage metals, of a series of dithiocarboxylato derivatives, whose IR spectra allow some interesting comparisons.

The differences in X-ray structures between the $[Au(S_2CAr)PPh_3]$ monomers and the corresponding $[Ag(S_2CAr)PPh_3]_2$ dimers [7] are paralleled by remarkable differences also in their IR spectra. In the former compounds the $\nu(CS_2)_{asym}$ is shifted to higher and the $\nu(CS_2)_{sym}$ to lower frequencies (Δ139–133 cm^{-1}) than in the latter (Δ106–103 cm^{-1}) and in the $[Au(S_2CAr)(PPh_3)_2]$ complexes (Δ101–91 cm^{-1}), reflecting the monodentate behaviour of the CS_2 group in the gold monophosphino derivatives. Furthermore, these complexes show a medium intensity doublet in the 538–505 cm^{-1} region, while the corresponding silver derivatives show a triplet in the 518–490 cm^{-1} region.

The spectra of the $[M(S_2CAr)(PPh_3)_2]$ complexes (M = Cu, Ag, Au) and of **III** are instead all corresponding for number and intensities of bands, with negligible variations in frequencies. They are hence characteristic of this stoichiometry, but scarcely influenced by variations in length of the M–S bonds.

The spectra of Cu(I), Ag(I) and Au(I) dithiocarboxylates do not follow a regular trend. The most intense absorption bands are those of the CS_2 group. The $\nu(CS_2)_{asym}$ peaks show about the same frequencies for silver and copper derivatives, but are at higher frequencies (Δ50–30 cm^{-1}) for gold dithiocarboxylates; the $\nu(CS_2)_{sym}$ peak is instead more intense, broader and shifted to lower frequencies (Δ20–15 cm^{-1}) for copper than for the other two metals. There is a rather good correspondence for the spectra of the phenyl and *p*-tolyl derivatives (limited for the latter to the region above 800 cm^{-1}) of copper and silver, but for the *o*-tolyldithiocarboxylates the best similarity is between the Au and Ag spectra and so strict to suggest a possible hexameric structure also for the Ag(I) dithiocarboxylate. Heteronuclear products between the silver and gold derivatives were, however, not obtained.

^{31}P NMR spectra

The phosphorous complexation shifts of the $[Au(S_2CAr)PPh_3]$ and $[Au(S_2CAr)(PPh_3)_2]$ complexes (Table 8) are in the usual range of the gold(I) mono and bisphosphino derivatives [32]. The noticeable increase found in the $[M(S_2CAr)(PPh_3)_2]$ compounds on moving from M = Cu [4] to M = Ag [7] to M = Au has to be attributed rather to 'heavy atom effects' than to differences in the strength of the metal–phosphorous interaction.

The ^{31}P NMR spectra of the $[Au(S_2CAr)PPh_3]$ complexes in $CD_2Cl_2/C_6H_5CH_3$ consist of a single narrow signal in the −100 to +40 °C temperature range, with chemical shifts almost independent of the temperature, i.e. the aryldithiocarboxylato monophosphino derivatives are stable in these solutions between −100 and +40 °C. In the dicoordinated $[AuXPR_3]$ compounds the phosphorous complexation shift depends noticeably on X, changing from 33 ppm in $[Au(NO)_3PPh_3]$ [33] to 44 ppm in $[Au(CN)PPh_3]$ [34a] to 49.5 ppm in $[Au(PPh_3)_2]^+$ [34a]. Thus the phosphorous δ values (Table 8(a)) suggest that the interaction of the triphenylphosphine with the molecular fragments $Au\text{-}S_2CAr$ and AuCN are analogous (as observed in the solid state for **I** and for $[Au(CN)PPh_3]$ reported by Bellon *et al.* [34b]), assuming that in the former the $ArCS_2$ retains also in solution the monodentate binding mode of the solid state.

TABLE 8. Selected NMR parameters for triphenylphosphine

Ar	C *ipso*	C *ortho*	C *meta*	C *para*	^{31}P	*K*
(a) $[Au(S_2CAr)PPh_3]$						
Ph	130.0	134.2	129.2	131.5_5	43	
	(55)	(14)	(12)	(2.5)		
p-T	130.0	134.2_5	129.2	131.5_5		
	(55)	(14)	(12)	(2.2)		
o-T	129.4	134.2	129.2	131.7	43	
	(60)	(13)	(12)	(2.2)		
Free PPh_3	137.4	133.8	128.5	128.6	0	
	(−11)	(19)	(7)			
(b) $[Au(S_2CAr)(PPh_3)_2]$						
Ph	133.9	134.0	128.5	130.2	43	0.06
	(40)					
p-T	133.9	134.0	128.5	130.1	42[a]	0.06
	(41)					
o-T	133.9	133.9	128.5	130.1	45	0.02
	(36)					
Free PPh_3	137.4	133.8	128.5	128.6	0	
	(−11)	(19)	(7)			

^{13}C δ values in ppm from TMS, splitting due to carbon–phosphorous coupling in Hz in parentheses, solvent $CDCl_3$, room temperature. ^{31}P δ values in ppm from PPh_3, solvent CD_2Cl_2–$C_6H_5CH_3$ (3:1), −100 °C. [a]Solvent CD_2Cl_2, −90 °C. In (b) the ^{13}C parameters and the constants for the dissociation equilibria $[Au(S_2CAr)(PPh_3)_2] \rightleftarrows [Au(S_2CAr)PPh_3] + PPh_3$ in $CDCl_3$ at 39 °C are calculated from the ^{13}C and ^{31}P spectra in the presence of excess phosphine by best fit procedures to the dependence of the peak positions on the phosphine concentration.

The $[Au(S_2CAr)(PPh_3)_2]$ compounds in CD_2Cl_2/$C_6H_5CH_3$ also give a single signal in the −100 to +40 °C temperature range, but the chemical shift and the linewidth depend heavily on the temperature. The low temperature complexation shifts (Table 8(b)) are weakly influenced by Ar, very close to the monophosphino complexes and smaller than the 49.5 ppm attributed to the $[Au(PPh_3)_2]^+$ ion [34a]. Thus in these solutions at low temperatures our bisphosphino compounds are present as tri- or tetra-coordinated molecules, with structures presumably similar to those reported here for the solid state.

Increasing the temperature the resonance moves to higher fields and its linewidth goes through a maximum (as an example for Ar=*o*-T: −100 °C, 12 Hz; −65 °C, 15 Hz; −30 °C, 40 Hz; 0 °C, 28 Hz; 41 °C, 10 Hz). This indicates that the molecules are thermodynamically stable only at low temperatures, the extent of dissociation

$$[Au(S_2CAr)(PPh_3)_2] \rightleftarrows [Au(S_2CAr)PPh_3] + PPh_3$$

becoming appreciable above −30 °C. Approximate values for the stoichiometric constants of this equilibrium, obtained from the NMR spectra, are reported in Table 8(b).

The triphenylphosphine exchanges rapidly and separate resonances for the $[Au(S_2CAr)PPh_3]$ and the $[Au(S_2CAr)(PPh_3)_2]$ species could be observed only for Ar=*o*-T below −90 °C. The exchange rate is remarkably enhanced in solutions containing $[Au(S_2CAr)(PPh_3)_2]$ and free PPh_3: at −90 to −100 °C the signals of the free and complexed phosphine, more than 1400 Hz apart, are very broad. Perhaps an associative mechanism involving a tristriphenylphosphino complex is operative, however, no evidence of stable tristriphenylphosphino compounds has been obtained.

The line shape is determined by the exchange rate, by the relative populations of the various species and by the differences in their chemical shifts. In a solution of $[Au(S_2CAr)(PPh_3)_2]$ at low temperatures this is the only species present and, even if the exchange is slow, a single narrow signal is observed. A temperature increase is paralleled by increases of the exchange rate and of the concentration of the free phosphine and the monophosphino complex. Appreciable concentrations of the latter species begin to be present (as inferred from the resonance position moving towards the free phosphine) at temperatures for which the exchange rate is high enough to give a single, even if rather broad, peak. At higher temperatures the exchange is faster, the improvement in the efficiency of the averaging process becomes the dominant factor and the signal becomes narrower.

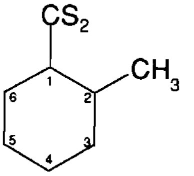
^{13}C and ^{1}H NMR spectra

Selected values for ^{13}C NMR parameters of the $[Au(S_2CAr)PPh_3]$ compounds are reported in Table 8(a) and 9. In the room temperature $^{13}C\{^1H\}$ spectra all the phosphine carbon signals are split into doublets by the coupling with phosphorous. Complexation with

TABLE 9. ^{13}C chemical shifts of $ArCS_2$ moieties

Compound	CS_2	C-1	C-2	C-3	C-4	C-5	C-6	Me
$[Au(S_2CPh)PPh_3]$	247.5	149.5	127.4	126.7	131.4	126.7	127.4	
$[Au(S_2C$-*p*-$T)PPh_3]$	246.8	146.8_5	128.0	126.9	142.2	126.9	128.0	21.4_5
$[Au(S_2C$-*o*-$T)PPh_3]$	252.9_5	155.8	130.8	127.4_5[d]	125.2_5[d]	125.1	130.3[d]	19.8
$[Au(S_2CPh)(PPh_3)_2]$[a]	250.6	151.4			130			
$[Au(S_2C$-*p*-$T)(PPh_3)_2]$[a]	249.5	148.5			140.6			
$[Au(S_2C$-*o*-$T)(PPh_3)_2]$[a]	256.5	156.2	131.2					
$PhCS_2$-NEt_4^+[b]	253.6	153.4	126.7	126.7	128.7	126.7	126.7	
p-TCS_2-NEt_4^+[b]	252.3	150.4	126.6	127.2	138.7	127.2	126.6	21.1

δ values in ppm from TMS, solvent $CDCl_3$, room temperature. The carbon numbers follow the scheme



[a]Calculated as in Table 8(b). [b]Ref 35. [d]Uncertain attribution.

the AuS_2CAr fragment causes remarkable changes in the *ipso* carbon resonances (the shielding increases by more than 7 ppm and the ^1J (^{13}C, ^{31}P) changes from -11 to 55–60 Hz) and in the *para* carbon resonances (the shielding decreases by about 3 ppm and the splitting due to coupling with phosphorous increases to about 2 Hz, becoming observable). The chemical shifts of the *ortho* and *meta* carbons are less affected, while the coupling with phosphorous is considerably changed, decreasing from 19 to 13–14 Hz for the former and increasing from 7 to 12 Hz for the latter. The directions of the variations are quite common for the reaction products between triphenylphosphine and Lewis acids; moreover their magnitudes imply that in the $[Au(S_2CAr)PPh_3]$ compounds the triphenylphosphine undergoes stronger modifications than in the other dithiocarboxylato complexes of the coinage metals [4, 7]. In particular the effect on the *para* carbon resonances reflects a considerable release of electronic charge from the phosphine phenyls; the effects on the *ipso* carbon are less straightforward to understand. The triphenylphosphine spectra of the phenyl and *p*-tolyl derivatives are identical, but significant, even if small, differences are found for the *o*-tolyl; this can be ascribed to the difference in the ligand properties of the CS_2 group when conjugated (phenyl, *p*-tolyl) or not with the aryl (*o*-tolyl).

Turning to the phenyl and *p*-tolyl dithiocarboxylate spectra the CS_2 and *ipso* carbons resonate at 5.5–6 ppm and at 3.5–4 ppm higher fields, respectively, and the *para* carbon at about 3 ppm lower fields than in the corresponding anions [35]. Comparisons with other aryldithiocarboxylato derivatives show that the effects on the CS_2 and *para* carbons are similar to those found in the $[Cu_4(S_2CAr)_4(PPh_3)_2]$ and $[Cu(S_2CAr)dppm]_2$ complexes [4] and stronger than those of the $[Ag(S_2CAr)(PPh_3)_2]$ complexes and that in the $[Au(S_2CAr)PPh_3]$ molecules there is a good amount of covalent character in the bonding between Au and $ArCS_2$ also in solution [35].

In the C_6D_6 ^1H spectra of the $[Au(S_2CAr)PPh_3]$ compounds the *ortho* proton multiplets of the $PhCS_2$ and *p*-TCS_2 moieties are centered at $\delta = 8.75$ ppm, i.e. these protons are strongly deshielded as already found in copper [36] and silver complexes [7]; the *ortho* proton of the *o*-TCS_2 moiety resonates at $\delta = 7.78$ ppm; this difference can be attributed to the different twist angles between the CS_2 and the aromatic ring.

In C_6D_6 the phosphine *ortho* protons give rise to a well resolved multiplet, separated from the *meta* and *para* proton resonances. The phenyl and *p*-tolyl derivatives give identical phosphine spectra. Homodecoupled spectra allowed us to establish that in the *p*-tolyl derivatives the $^3J(^{31}P,^1H)$ is 12 Hz, i.e. noticeably higher than the 7.3 Hz of the free phosphine [37]. In the $[Ag(S_2CAr)(PPh_3)_2]$ complexes this coupling constant is also higher than in the free ligand.

The ^{13}C parameters of the $[Au(S_2CAr)(PPh_3)_2]$ compounds reported in Tables 8(b) and 9 were calculated together with the equilibrium constants from the spectra of solutions containing various excesses of phosphine, which gave also clear evidence for the different sign of ^1J (^{13}C,^{31}P) in the free and complexed phosphine as, for appropriate ratios of these species, it was possible to get spectra without splitting. The complexation shifts of the PPh_3 *ipso* and *para* carbons are comparable to those of the $[Cu_4(S_2CAr)_4(PPh_3)_2]$, $[Cu(S_2CAr)(PPh_3)_2]$ [4] and $[AgS_2CAr(PPh_3)_2]$ [7] compounds, suggesting that all these molecules have analogous metal–

phosphine interactions. These values are nearly one half of those found for the [Au(S_2CAr)PPh_3] complexes and reflect a weaker coordination of PPh_3 in the bis- than in the mono-phosphino gold derivatives, which is in line with the Au–P bond being longer for **II** than for **I** in the solid state (Tables 6 and 7). Also the CS_2, *ipso* and *para* carbons of the ArCS_2 moieties show complexation shifts about halved with respect to the monophosphino derivatives. The P–Au–P angle much smaller than 180°, the difference of the length of the two C–S bonds in **II**, and the difference between the carbon chemical shifts of the ArCS_2 moiety and those of the anion show that the bonding between Au and ArCS_2 in the bisphosphino complexes retains some covalent character both in the solid state and in $CDCl_3$ solution. The Au–S distances and the magnitude of the ArCS_2 moiety complexation shifts indicate that this covalence is noticeably weaker than in the monophosphino gold derivatives. The CS_2 and *para* carbon complexation shifts suggest that the ArCS_2 interaction with the metal in the [Au(S_2CAr)$(PPh_3)_2$] compounds is comparable with that in [Ag(S_2CAr)$(PPh_3)_2$], but weaker than in the [Cu(S_2CAr)dppm$]_2$ derivatives. Perhaps the C *ipso* complexation shift has a strong dependence on the specific binding mode of CS_2.

Supplementary material

Listing of observed and calculated structure factors, thermal anisotropic parameters and fractional coordinates of the hydrogen atoms are available from the authors on request.

Acknowledgements

This work was supported by the Italian MURST. We thank Dr E. Cebulec for the elemental analyses and Mr P. de Baseggio for recording the IR spectra.

References

1 A. M. Manotti Lanfredi, F. Ugozzoli, A. Camus and N. Marsich, *Inorg. Chim. Acta, 99* (1985) 111.

2 A. M. Manotti Lanfredi, A. Tiripicchio, N. Marsich and A. Camus,*Inorg. Chim. Acta, 142* (1988) 269.

3 A. M. Manotti Lanfredi, A. Tiripicchio, A. Camus and N. Marsich, *J. Chem. Soc., Dalton Trans.,* (1989) 753.

4 G. Pellizer, N. Marsich and A. Camus, *Inorg. Chim. Acta, 155* (1989) 167.

5 A. Camus, N. Marsich, A. M. Manotti Lanfredi and F. Ugozzoli, *Inorg. Chim. Acta, 161* (1989) 87.

6 N. Marsich, G. Pellizer, A. Camus, A. M. Manotti Lanfredi and F. Ugozzoli, *Inorg. Chim. Acta, 169* (1990) 171.

7 A. M. Manotti Lanfredi, F. Ugozzoli, F. Asaro, G. Pellizer, N. Marsich and A. Camus, *Inorg. Chim. Acta, 190* (1991) 71.

8 A. Camus, N. Marsich, A. M. Manotti Lanfredi and F. Ugozzoli, *Inorg. Chim. Acta, 175* (1990) 193.

9 X. Jin, K. Tang, Y. Han, A. Camus and N. Marsich, *J. Coord. Chem., 22* (1990) 1.

10 K. Tang and Y. Tang, in E. Block (ed.), *Heteroatom Chemistry,* VCH, New York, 1990, p. 345, and refs. therein.

11 J. A. Schuerman, F. R. Fronczek and J. Selbin, *J. Am. Chem. Soc., 108* (1986) 336.

12 B. Chiari, O. Piovesana, T. Tarantelli and P. F. Zanazzi, *Inorg. Chem., 24* (1985) 366.

13 S. J. Bernes-Price and P. J. Sadler, *Struct. Bonding (Berlin) 70* (1988) 27.

14 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A, 30* (1974) 580.

15 F. Ugozzoli, *Comput. Chem., 11* (1987) 109.

16 G. M. Sheldrick, *SHELX76 and SHELX86,* system of computing programs, University of Cambridge, UK, 1976 and 1986.

17 *International Tables for X-ray Crystallography,* Vol. 4, Kynoch, Birmingham, UK, 1974.

18 M. Nardelli, *Comput. Chem., 7* (1983) 95.

19 C. Rizzoli, V. Sangermano, G. Calestani and G. D. Andretti, *J. Appl. Crystallogr., 20* (1987) 436.

20 F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rodgers and D. G. Watson, *Acta Crystallogr., Sect. B, 35* (1979) 2331.

21 J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin and W. C. Seidel, *J. Am. Chem. Soc., 90* (1978) 2784.

22 J. G. Wijnhoven, W. P. J. H. Bosman and P. T. Beurskens, *J. Cryst. Mol. Struct., 2* (1972) 7.

23 H. M. Colquhoun, T. J. Greenhough and M. G. H. Walbridge, *J. Chem. Soc., Dalton Trans.,* (1978) 303; R. Uson, A. Laguna, M. Laguna, M. L. Castilla, P. G. Jones and K. Meyer-Base, *J. Organomet. Chem., 336* (1987) 453; H. H. Murray, G. Garzon, R. G. Raptis, A. M. Mazany, L. C. Porter and J. P. Fackler, Jr., *Inorg. Chem., 27* (1988) 836.

24 F. A. Cotton, L. R. Falvello, C. A. Murillo and G. Valle, *Z. Anorg. Allg. Chem., 540/541* (1986) 67.

25 J. H. Noordik and P. T. Beurskens, *J. Cryst. Mol. Struct., 1* (1971) 339, and refs. therein.

26 J. A. Muir, M. M. Muir and S. Arias, *Acta Crystallogr., Sect. A, 37* (1981) C227.

27 J. A. Muir, M. M. Muir, S. Arias, C. F. Campana and S. K. Dwight, *Acta Crystallogr., Sect. B, 38* (1982) 2047.

28 A. L. Balch and E. Y. Fung, *Inorg. Chem., 29* (1990) 4764.

29 S. J. Berners-Price and P. J. Sadler, *Chem. Br., 23* (1987) 541.

30 J. A. Muir, M. M. Muir and S. Arias, *Acta Crystallogr. Sect., B, 38* (1982) 1318.

31 L. J. Guggenberger, *J. Organomet. Chem., 81* (1974) 271.

32 C. B. Colburn, W. E. Hill, C. A. McAuliffe and R. V. Parish, *J. Chem. Soc., Chem. Commun.,* (1979) 218; S. Al-Baker, W. E. Hill and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.,* (1986) 1297.

33 F. A. Vollenbroek, J. P. van den Berg, J. W. A. van der Velden and J. J. Bour, *Inorg. Chem., 19* (1980) 2685.

34 (a) A. L. Hormann-Arendt and C. F. Shaw III, *Inorg. Chem., 29* (1990) 4683; (b) P. L. Bellon, M. Manassero and M. Sansoni, *Ric. Sci., 39* (1969) 173.

35 T. Roberie, N. S. Baccha, D. Lankin and J. Selbin, *Can. J. Chem., 58* (1980) 2314.

36 A. Camus, N. Marsich and G. Pellizer, *J. Organomet. Chem., 259* (1983) 367.

37 S. Sorensen and H. J. Jacobsen, *Acta Chem. Scand., Ser. A, 28* (1974) 249.