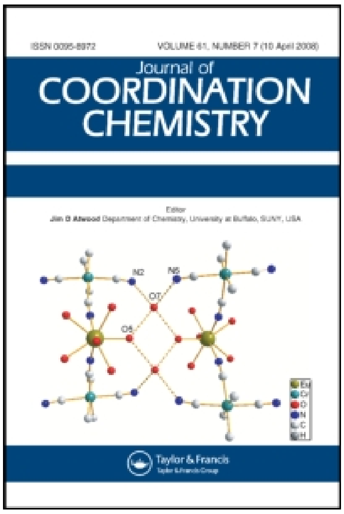

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SYNTHESES AND STRUCTURAL STUDIES OF TRIORGANOPHOSPHINEGOLD(I) MERCAPTOBENZOATE COMPLEXES

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Compounds of the type $R_3PAu(SC_6H_4CO_2H)$, R = Et, Ph or c-hexyl have been prepared and characterized by IR, ^1H and ^{13}C NMR and FAB MS spectroscopic techniques. The Au atom has been shown to be linearly coordinated by the R_3P ligand and the S atom of the thiolate; there is no interaction between the carboxylic acid function and the Au atom. These results were verified by a crystal structure analysis of the R = c-hexyl derivative which showed the Au atom to exist in a linear geometry with Au–S 2.313(1), Au–P 2.271(1) Å and S–Au–P 176.8(1)°. The c-hexyl$_3$PAu($SC_6H_4CO_2H$) compound crystallizes in the triclinic space group $P\bar{1}$, with unit cell dimensions $a = 11.048(2)$, $b = 13.752(1)$, $c = 9.858(1)$ Å, $\alpha = 107.72(1)$, $\beta = 97.99(1)$, $\gamma = 111.46(1)°$ and $Z = 2$. The structure has been refined to final $R = 0.036$ and $R_w = 0.036$ for 4849 reflections with $I \geqslant 2.5\sigma(I)$.

Keywords: Gold(I), phosphine, mercaptobenzoate, X-ray structure

INTRODUCTION

Polymeric gold(I) thiolates $[AuSR]_n$ and monomeric phosphinegold(I) thiolates R_3PAuSR' are employed in the treatment of rheumatoid arthritis[1,2] and hence there has been a resurgence of interest in the chemistry of gold. Among the commercially available drugs is Auranofin, (1-thio-β-D-glucopyranose 2,3,4,6-tetraacetato-*S*)-(triethylphosphine)gold(I), which features a linear P–Au–S entity.[3] As a part of a study of related R_3PAuSR' species where both the R groups of the phosphine and the nature of the thiolate are varied, the title compounds, $R_3PAu(SC_6H_4CO_2H)$, R = Et, Ph or c-hexyl, have been investigated. In connection with their putative anti-arthritic activity, compounds of this type have been reported in the patent literature;[4,5] however, no details of their characterization or chemistry have been published. This paper reports the spectroscopic characterization (IR, NMR and FAB MS) of $R_3PAu(SC_6H_4CO_2H)$, R = Et, Ph or c-hexyl, and the X-ray crystal structure of the R = c-hexyl derivative.

EXPERIMENTAL

Instrumentation

IR spectra were measured on a Perkin Elmer 1720X FT spectrometer, in KBr discs, calibrated using the polystyrene absorption at 1601.4 cm^{-1}. NMR spectra were

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recorded in d_6-dmso solutions on an ACP300 (^{1}H NMR at 300.13 MHz and ^{13}C NMR at 75.47 MHz) spectrometer; the internal reference was $SiMe_4$ in both cases. FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas with the source pressure typically 10^{-6} mbar, the FAB voltage was 7 kV and the current 1 mA. The ion accelerating potential was 8 kV and the matrix employed was 3-nitrobenzyl alcohol. The complexes were made up as *ca* 0.5 mol dm^{-3} solutions in dichloromethane; a drop was added to a drop of the matrix and the mixture was applied to the FAB probe tip.

Preparations

$Et_3PAu(SC_6H_4CO_2H)$ was prepared from the equimolar reaction of Et_3PAuCl[6] (200 mg, 0.572 mmol), 2-mercaptobenzoic acid (Fluka) and KOH in aqueous ethanolic solution. The solution was stirred for 0.5 h, filtered and allowed to evaporate under ambient conditions. The precipitate thus obtained was recrystallized from acetone solution to yield colourless crystals; yield: 86%, m.p. 109–110°C, lit.[4] 109.5–110°C, found: C, 33.49; H, 4.44%. $C_{13}H_{20}AuO_2PS$ requires C, 33.34; H, 4.30%. The R = Ph (yield: 63%, m.p. 149–150°C, found: C, 49.36; H, 3.29%. $C_{25}H_{20}AuO_2PS$ requires C, 49.03; H, 3.29%) and R = c-hexyl (yield: 60%, m.p. 156–157°C, found: C, 48.61; H, 6.40%. $C_{25}H_{38}AuO_2PS$ requires C, 47.62; H, 6.07%) compounds were prepared employing the same procedure as for R = Et.

Crystallography

Intensity data for a transparent crystal of c-hexyl$_3$PAu($SC_6H_4CO_2H$), 0.12 × 0.12 × 0.62 mm, grown by the vapour diffusion of ether into an ethanol solution of the compound, were measured at room temperature on an Enraf-Nonius CAD4*F* diffractometer with Mo $K\alpha$ radiation (graphite monochromator), $\lambda = 0.7107$ Å. The ω:2θ scan technique was employed to measure the intensities of 6755 reflections up to a maximum Bragg angle of 27.5°. The data set was corrected for Lorentz and polarization effects and an analytical absorption correction was also applied[7] such that the maximum and minimum transmission factors were 0.470 and 0.311, respectively. Crystal data are summarized in Table I.

The structure was solved from the interpretation of the Patterson map and refined by a full-matrix least-squares procedure based on F.[7] Non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the model at their calculated positions; the position of the carboxylic acid H atom, H(2), was located from a difference map but its position not refined. A weighting scheme of the form $w = [\sigma^2(F) + |g|F^2]^{-1}$ was introduced and the refinement continued until convergence; final refinement details are listed in Table I. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied. Fractional atomic coordinates are listed in Table II and the numbering scheme employed is shown in Figure 1 which was drawn with ORTEP[8] at 15% probability ellipsoids. Scattering factors for neutral Au (corrected for f' and f'') were from the *International Tables for X-ray Crystallography*[9] while those for the remaining atoms were those incorporated in SHELX76.[7] Refinement was performed on a SUN4/280 workstation. Listings of thermal parameters, H atom parameters, all bond distances and angles, and structure factor amplitudes are available on request from the authors.

TABLE I
Crystal data and refinement details for c-hexyl$_3$PAu(SC$_6$H$_4$CO$_2$H).

Formula	$C_{25}H_{38}AuO_2PS$
Formula weight	630.6
Crystal system	triclinic
Space group	$P\bar{1}$, (C_i^1, No. 2)
a(Å)	11.048(2)
b(Å)	13.752(1)
c(Å)	9.858(1)
α(°)	107.72(1)
β(°)	97.99(1)
γ(°)	111.46(1)
V(Å^3)	1273.7
Z	2
D_{calcd}(g cm^{-3})	1.644
F(000)	628
μ(mm^{-1})	5.891
No. of data collected	6755
No. of unique data	5853
No. of data with $I \geqslant 2.5\sigma(I)$	4849
R	0.036
g	0.0028
R_w	0.036

RESULTS AND DISCUSSION

The complexes, R$_3$PAu(SC$_6$H$_4$CO$_2$H), R = Et, Ph or c-hexyl, were prepared by the reaction between R$_3$PAuCl and HSC$_6$H$_4$CO$_2$H in the presence of base. The colourless products are crystalline, air stable solids and have been characterized by IR, NMR and FAB MS spectroscopy and in the case of the R = c-hexyl compound, by single-crystal X-ray diffraction methods.

Selected IR data, recorded in KBr discs, are listed in Table III. The spectrum of the ligand shows an absorption at 2527 cm^{-1}, assigned to ν(S–H), which is absent in the spectra of the complexes suggesting the deprotonation of the thiol and therefore implies the coordination of the S atom to the Au atom. Small shifts to lower frequency are found for the ν(C–S) bands (1028–1054 cm^{-1}) in the spectra of the complexes compared to the free ligand, however, no clear trends are found in the ν_{asymm}(COO) and ν_{sym}(COO) regions of the spectra for both the ligand and complexes (Table III).

The ^{1}H and ^{13}C NMR results, obtained in d_6-dmso solution, are summarized in Table IV. Our experience has shown that NMR spectra of phosphinegold(I) thiolates of this type recorded in d_6-dmso solution are similar to those obtained in chlorinated solvents suggesting no interaction between the complex and the solvent; d_6-dmso was chosen as the solvent for this study owing to the limited solubility of the complexes in solvents such as CDCl$_3$ for the ^{13}C NMR spectra. The carboxylic acid H atom (and the S*H* atom in the free ligand) was not observed in any of the spectra. The

TABLE II

Fractional atomic coordinates (× 10^5 for Au; × 10^4 for remaining atoms) for c-hexyl$_3$PAu(SC$_6$H$_4$CO$_2$H).

Atom	x/a	y/b	z/c
Au	29067(2)	2693(1)	5737(2)
S(2)	1306(1)	−1596(1)	−328(2)
P(1)	4548(1)	2078(1)	1549(1)
O(1)	160(4)	−3887(3)	−400(4)
O(2)	−430(4)	−4211(3)	1524(4)
C(1)	−290(4)	−2520(3)	1338(4)
C(1′)	−161(4)	−3598(3)	728(4)
C(2)	327(4)	−1581(3)	948(4)
C(3)	111(4)	−620(3)	1578(5)
C(4)	−620(5)	−561(4)	2596(5)
C(5)	−1221(5)	−1471(4)	2986(5)
C(6)	−1050(4)	−2438(4)	2353(5)
C(11)	6180(4)	2190(3)	2537(4)
C(12)	7142(4)	3367(4)	3747(5)
C(13)	8496(5)	3374(5)	4398(5)
C(14)	8281(5)	2445(5)	4980(5)
C(15)	7309(5)	1288(4)	3796(5)
C(16)	5964(4)	1270(4)	3179(5)
C(21)	4873(4)	2640(3)	94(4)
C(22)	5170(5)	1836(4)	−1129(5)
C(23)	5324(5)	2222(4)	−2428(5)
C(24)	6352(5)	3431(4)	−1918(5)
C(25)	6045(5)	4212(4)	−716(5)
C(26)	5955(5)	3854(3)	611(5)
C(31)	4032(3)	3016(3)	2847(4)
C(32)	3730(4)	2622(3)	4113(4)
C(33)	3280(4)	3398(4)	5183(5)
C(34)	2036(4)	3445(4)	4378(5)
C(35)	2324(4)	3837(4)	3120(5)
C(36)	2803(4)	3090(4)	2041(5)

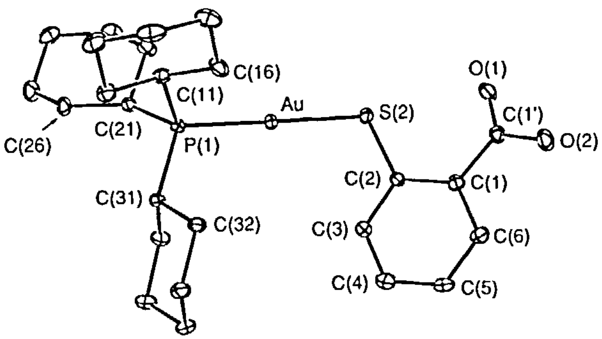

FIGURE 1 Molecular structure and crystallographic numbering scheme for c-hexyl$_3$PAu(SC$_6$H$_4$CO$_2$H).

TABLE III
Significant bands (cm^{-1}) in the IR spectra of the ligand and $R_3PAu(SC_6H_4CO_2H)$ complexes.

Compound	ν_{asym}(COO)	ν_{sym}(COO)	ν(C-S)
$HSC_6H_4CO_2H$	1682s, 1654sh	1418s	1066m 1044m
R=Et	1678s, 1652m	1385m	1054m 1034m
R=Ph	1683s, 1663m	1385m	1053m 1036m 1028m
R=c-hexyl	1718s, 1635m	1385s	1047m 1036m

TABLE IV
^{1}H and ^{13}C NMR results[a] for the ligand and $R_3PAu(SC_6H_4CO_2H)$ complexes.

^{1}H NMR	H3	H4	H5	H6	Hα	Hβ	Hγ	Hδ
$HSC_6H_4CO_2H$	8.01 dd J_{HH} 7.74 $^4J_{HH}$ 1.13	7.48 dt J_{HH} 7.42 $^4J_{HH}$ 1.29	7.27 t J_{HH} 7.45	7.62 d J_{HH} 8.17				
R=Et	7.70 d J_{HH} 7.79	7.12 t J_{HH} 7.55	6.96 t J_{HH} 7.44	7.37 d J_{HH} 7.57	1.11 dt J_{HH} 7.59 J_{PH} 10.02	1.91 m J_{HH} 7.44 J_{PH} 18.69		
R=Ph	7.81 d J_{HH} 7.82	7.12 t J_{HH} 7.58	7.01 t J_{HH} 7.58	b	c			
R=c-hexyl	7.65 d J_{HH} 7.74	7.08 dt J_{HH} 7.61 $^4J_{HH}$ 1.49	6.93 dt J_{HH} 7.40 $^4J_{HH}$ 0.81	7.32 dd J_{HH} 7.59	2.15 m J_{HH} 10.85 J_{PH} 1.94	1.78 m J_{HH} 8.92	1.66 m J_{HH} 10.74	

^{13}C NMR	C1	C1′	C12	C13	C14	C15	C16	Cα	Cβ	Cγ	Cδ
$HSC_6H_4CO_2H$	133.4	167.9	139.3	131.8	126.1	125.2	128.3				
R=Et	135.3	169.7	142.7	134.7	128.5	122.7	128.8	17.0 J_{PC} 33.9	9.0		
R=Ph	135.6	169.8	142.2	135.2	b	123.3	b	128.8 to 135.2			
R=c-hexyl	136.4	169.9	142.2	134.4	128.2	122.7	128.5	32.4 J_{PC} 28.3	26.4 J_{PC} 12.0	30.3	25.5

[a] Spectra measured in d_6-dmso, resonances reported in p.p.m., and coupling constants reported in Hz. [b] Obscured by phenyl H (or C for ^{13}C NMR) atoms. [c] Resonances in the range 7.25–7.68 p.p.m.

^{1}H spectra showed the expected resonances and integration for the different H atoms consistent with the $R_3PAu(SC_6H_4CO_2H)$ formulation. Upon coordination to the Au atom all ligand ^{1}H resonances are shifted upfield, a trend that has been observed previously for *S*-bonded 2-mercapto-pyrimidine complexes.[10] For the R=Et and c-hexyl compounds, characteristic couplings are observed for the H atoms proximate to the P atom (Table IV). The ^{13}C spectra of the complexes also show a general downfield shift upon coordination; the only exception being for the C(5) atom, which is shifted upfield (the numbering scheme employed is as shown in Figure 1). It is noted, however, that the differences in the resonances for the C(6) atom in the ligand and complexes are small. There are only small changes in the position of the CO_2 resonances which may imply the presence of the carboxylic acid function in solution for the complexes.

The FAB MS spectra of the complexes, summarized in Table V, show the presence of the molecular ion $[R_3PAu(SC_6H_4CO_2H)]^+$, $[M]^+$, in each case. The most significant fragment of $[M]^+$ in the spectra corresponds to the mononuclear $[R_3PAu]^+$ ion. More interesting, however, are the high molecular weight regions which display peaks corresponding to high nuclearity ions arising from recombination of the $[R_3PAu]^+$ ion with $[M]^+$ and the cleavage of the S–C bond(s). Thus, in addition to the $[(R_3PAu)_2(SC_6H_4CO_2H)]^+$ species, peaks corresponding to the $[(R_3PAu)_2S]^+$, $[(R_3PAu)_2AuS]^+$, and $[(R_3PAu)_3S]^+$ ions are found. It is noteworthy that peaks with the thiolate ligand intact occur in a significantly higher relative abundance for the R = Et compound compared to the R = Ph or c-hexyl compounds.

The spectroscopic evidence indicates the presence of a thiolate ligand coordinating the R_3PAu entity *via* the S atom exclusively and the non-participation of the carboxylic acid function in coordination to the Au atom. These results have been confirmed for the R = c-hexyl compound for which suitable crystals were obtained for an X-ray crystallographic study.

The molecular structure of c-hexyl$_3$PAu(SC$_6$H$_4$CO$_2$H) is shown in Figure 1 and selected interatomic parameters are listed in Table VI. The Au atom exists in the expected linear geometry defined by the S (Au–S(2) 2.313(1) Å) and P (Au–P(1) 2.271(1) Å) atoms such that the S(2)–Au–P(1) angle is 176.8(1)°; the carboxylic acid group is directed away from the Au atom. The Au–S bond distance is equal within experimental error to the Au–S distance of 2.310(2) Å found in the closely related Et_3PAu(2-TU) (2-TUH is 2-thiouracil) compound[11] and is marginally longer than the two independent Au–S distances of 2.296(2) and 2.300(2) Å in the Ph_3PAu(2-TU) analogue (two crystallographically independent molecules)[12] and the Au–S distance of 2.299(2) Å in Ph_3PAu(Sboz) (HSboz is 2-mercaptobenzoxazole).[13] It is noteworthy that the Au–P(1) bond distance in c-hexyl$_3$PAu(SC$_6$H$_4$CO$_2$H) is significantly longer at 2.271(1) Å than the Au–P bond distances of 2.248(2) for the three R_3PAu(2-TU) molecules[11,12] and 2.258(2) Å in the Ph_3PAu(Sboz) compound.[13] This may reflect

TABLE V

Significant fragments in the FAB MS spectra of the $R_3PAu(SC_6H_4CO_2H)$ complexes.

	R = Et		R = Ph		R = c-hexyl	
Fragment	M	%	M	%	M	%
$[R_3PAu]^+$	315	80	459	100	477	100
$[(R_3P)_2Au]^+$	433	100	721	23	757	46
$[R_3PAu(SC_6H_4CO_2H)]^+ \equiv [M]^+$	469	84	612	20	631	15
$[(R_3PAu)_2S]^+$	662	32	950	5	986	13
$[(R_3PAu)_2(SC_6H_4CO_2H)]^+$	783	100	1071	8	1107	20
$[(R_3PAu)_2AuS]^+$	859	21	1147	3	1183	6
$[(R_3PAu)_3S]^+$	977	84	1409	10	1463	41

TABLE VI
Selected bond distances (Å) and angles (°) for c-hexyl$_3$PAu(SC$_6$H$_4$CO$_2$H).

Au-S(2)	2.313(1)	Au-P(1)	2.271(1)
S(2)-C(2)	1.769(4)	P(1)-C(11)	1.855(4)
P(1)-C(21)	1.844(4)	P(1)-C(31)	1.834(4)
C(1)-C(2)	1.418(6)	C(1)-C(1′)	1.489(6)
C(1′)-O(1)	1.209(5)	C(1′)-O(2)	1.303(5)
C(1)-C(6)	1.398(6)	C(2)-C(3)	1.402(6)
C(3)-C(4)	1.374(7)	C(4)-C(5)	1.383(7)
C(5)-C(6)	1.381(7)		
S(2)-Au-P(1)	176.8(1)	Au-S(2)-C(2)	102.8(1)
Au-P(1)-C(11)	112.0(1)	Au-P(1)-C(21)	111.4(1)
Au-P(1)-C(31)	110.8(1)	C(11)-P(1)-C(21)	107.2(2)
C(11)-P(1)-C(31)	108.6(2)	C(21)-P(1)-C(31)	106.6(2)
S(2)-C(2)-C(1)	122.8(3)	S(2)-C(2)-C(3)	119.4(3)
C(1)-C(2)-C(3)	117.8(4)	C(2)-C(1)-C(1′)	123.2(4)
C(2)-C(1)-C(6)	119.1(4)	C(1′)-C(1)-C(6)	117.7(4)
C(1)-C(1′)-O(1)	123.6(4)	C(1)-C(1′)-O(2)	113.7(4)
O(1)-C(1′)-O(2)	122.7(4)		

the greater cone-angle of the c-hexyl$_3$P ligand, *i.e.*, 170°, compared to those of the Et$_3$P and Ph$_3$P ligands of 132 and 145°, respectively.[14] Comparisons between the complexes is difficult, however, as the thiolate ligand is varied across this series. Definitive conclusions can not be made.

The SC$_6$H$_4$CO$_2$H fragment is not planar. Whereas the C$_6$S atoms are planar to within $\pm 0.018(5)$ Å, the CO$_2$H group forms a dihedral angle of 19.3° with this plane showing that little delocalization of π-electron density occurs between the SC$_6$H$_4$ and CO$_2$H moieties. The difference in the C(1′)-O bond distances, *i.e.*, 1.209(5) Å and 1.303(5) Å, shows that the O(2) atom is protonated.

In the crystal lattice of c-hexyl$_3$PAu(SC$_6$H$_4$CO$_2$H) there are few significant intermolecular interactions. The most important interaction is illustrated in Figure 2 for the association between two centrosymmetrically related molecules *via* the carboxylic acid moieties leading to the formation of a dimeric unit. The O(2)-H(2)...O(1)′ (symmetry operation: $-x$, $1-y$, $-z$) separation is 1.71(1) Å and the O(2)-H(2)...O(1)′ angle is 166(1)°. The closest Au...Au″ (symmetry operation: $1-x$, $-y$, $-z$) interaction in the lattice is 5.165(2) Å.

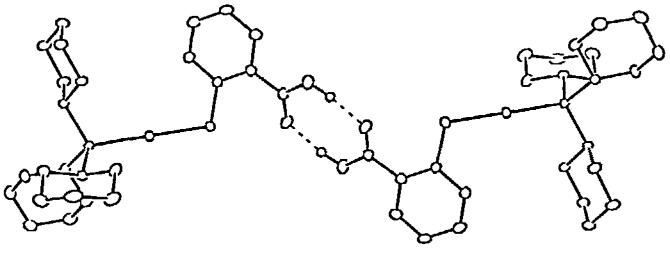

FIGURE 2 Centrosymmetric dimers in the crystal structure of c-hexyl$_3$PAu(SC$_6$H$_4$CO$_2$H).

There are several other crystal structures available in the literature containing anions derived from $HSC_6H_4CO_2H$. An Hg complex, $Hg(SC_6H_4CO_2H)_2$.dioxane,[15] has the Hg atom situated on a centre of inversion being coordinated by two S atoms (Hg–S 2.361(7) Å, S–C 1.76(2) Å). The $Hg(SC_6H_4CO_2H)_2$ units are linked *via* hydrogen bonds between the carboxylic acid residues and the dioxane molecules leading to a zig-zag chain. A doubly deprotonated ligand has been characterized in the structures of $[NEt_4][Me_2Sn(SC_6H_4CO_2)Cl]$,[16] the trinuclear complex $[NHEt_3]_2[Mo_3S(S_2)_3(SC_6H_4CO_2)_3]$,[17] and in the dinuclear triorganotin complex $Ph_3Sn(SC_6H_4CO_2)SnPh_3$.[18] The $SC_6H_4CO_2$ dianion chelates the Sn atom *via* the S (Sn–S 2.422(3) Å) and one O atom (Sn–O 2.191(7) Å) in the $[Me_2Sn(SC_6H_4CO_2)Cl]^-$ anion,[16] a similar chelation mode is found for each of the $SC_6H_4CO_2$ dianions in the $[Mo_3S(S_2)_3(SC_6H_4CO_2)_3]^{2-}$ dianion.[17] In the structure of $Ph_3Sn(SC_6H_4CO_2)SnPh_3$[18] one of the Sn atoms is bonded to the thiolate (Sn–S 2.414(1), S–C 1.781(4) Å) and the other Sn atom is coordinated to one of the carboxylate O atoms (Sn–O 2.079(3) Å); the second O atom is separated by 2.765(3) Å from the Sn atom and is not considered to indicate a significant bonding contact to the Sn atom.[18]

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