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Mixed ligand gold(I) complexes of phosphines and thiourea and X-ray structure of (thiourea-κS)(tricyclohexylphosphine)gold(I)chloride

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Abstract

A series of mixed ligand gold(I) complexes with thiourea (Tu) and various phosphines, [R_3PAuTu]Cl, have been prepared and characterized by elemental analysis, IR and NMR (^{13}C, ^{15}N and ^{31}P) spectroscopies and X-ray crystallography. The spectral data of all complexes are consistent with the sulfur coordination of thiourea to gold(I). The single crystal X-ray structure of the complex [Cy_3P–Au–Tu]Cl revealed that the geometry is not perfectly linear at the gold(I) with a P–Au–S bond angle of 168.54(9)°. The Au–P and Au–S distances are 2.274(2) and 2.295(2) Å, respectively.

Keywords: Gold(I) complexes; X-ray structures; Thiourea

1. Introduction

Recent interest in gold(I) complexes with sulfur and phosphorus donor ligands was stimulated by the anti-arthritic properties exhibited by some gold compounds like myocrisin, solganol and auranofin [1,2].

Thiourea (Tu) and imidazolidine-2-thione and its derivatives are simple sulfur containing ligands and thus gold(I) complexes of thiourea are expected to form useful additional new compounds, which may serve as models for presently available therapeutic agents. The ability of thiourea (Tu) to form stable adducts with a variety of transition metals (Cu, Ag, Au and Pt) is well established and the structures of several such complexes have been determined [3–11].

We have been interested in the spectral and structural chemistry of gold–phosphorus and gold–sulfur interactions involving phosphines, heterocyclic thiones and thiolates [11–13]. We have also studied the solution equilibria of cyanogold(I) complexes for a series of phosphines, thiones and selenones [14,15]. As a part of our continuing research program in this area, here we report the synthesis and characterization of phosphine–gold(I) complexes of thiourea.

2. Experimental

2.1. Chemicals

Thiourea, MeOD, NH_4NO_3, Me_2S and all solvents were obtained from the Fluka–Aldrich Chemical Co., Germany. ^{13}C and ^{15}N labelled (~98% each atom) thiourea was obtained from Isotec Co, USA. $HAuCl_4 \cdot 3H_2O$ and all phosphines were obtained from the Strem Chemical Co.

2.2. Synthesis of the complexes

All [R_3PAuTu]Cl complexes were prepared by the addition of thiourea to the corresponding precursor complexes, R_3PAuCl. The R_3PAuCl complexes were prepared by adding phosphines to the slurry of Me_2S–AuCl in acetone under N_2 and stirring for half an hour

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[11]. The labelled thiourea was mixed with unlabelled thiourea to give ~10% ^{13}C and ^{15}N labelled thiourea.

The phosphines used in the study were; Me_3P, Et_3P, Ph_3P, Cy_3P, $CyPh_2P$, $(o\text{-Tol})_3P$, $(m\text{-Tol})_3P$, $(p\text{-Tol})_3P$ (where Cy = cyclohexyl, Tol = tolyl).

2.2.1. Preparation of [Ph$_3$PAuTu]Cl

[Ph_3PAuCl] (0.494 g, 1 mmol) was dissolved in 20 cm^3 of MeOH. Thiourea (0.076 g, 1 mmol) was added as a solid to the solution. The solution was stirred for 15–20 min. The resulting colorless solution was filtered and kept in a refrigerator at 4 °C for crystallization. A total of 0.394 g of the product was obtained corresponding to 69% after crystallization.

A similar procedure was followed for the rest of the syntheses where [R_3PAuTu]Cl complexes were first dissolved in MeOH or acetone followed by addition of 1 equivalent of solid thiourea into the solution. As a result, white crystalline products were obtained in 60–70% yield. The complex [$(m\text{-Tol})_3PAuTu$]Cl was prepared in acetonitrile and [$(CyPh_2)PAuTu$]Cl was isolated from a mixture of acetone and hexane. The complex [$(p\text{-Tol})_3PAuTu$]Cl could not be isolated in the solid state and therefore it was studied by preparing it in the solution form. The elemental analysis, % yield, m.p., etc. of these complexes are given in Table 1.

2.3. X-ray data collection and structure determination

A colorless needle-shaped crystal of the complex [Cy_3PAuTu]Cl was mounted on a glass fiber. Data collection was performed on a kappa CCD four circle Enraf–Nonius diffractometer, equipped with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz and polarization effects. Effective absorption correction was performed (SCALEPACK) [16] and the structure was solved and refined by full-matrix least-squares method, on F^2, using SHELXS-97 and SHELXL-97, respectively [17,18]. Crystallographic data are given in Table 2. Hydrogen atoms were included at calculated positions with isotropic thermal parameters proportional to those of the connected atoms. For the NH_2 groups, a planar geometry was assumed for the $S{=}C(NH)_2$ moiety. Selected bond lengths and angles are given in Table 3. Complete bond lengths and bond angles, anisotropic thermal parameters and calculated hydrogen coordi-

Table 2
Crystallographic data for [$Cy_3P{-}Au{-}Tu$]Cl

Formula	[$C_{19}H_{37}N_2PSAu$]Cl
F_w	588.95
Crystal system	orthorhombic
Space group	$Pna2_1$
T (K)	293(2)
λ (Å)	0.71073
ρ_{calc} (g cm^{-3})	1.676
μ (mm^{-1})	6.582
$F(000)$	1168
Unit cell dimensions	
a (Å)	16.8506(2)
b (Å)	16.9731(5)
c (Å)	8.1590(5)
V (Å^3)	2333.5(2)
Z	4
θ range (°)	2.40–27.47
Index ranges	$-21 \le h \le 21$, $-21 \le k \le 22$, $-10 \le l \le 10$
No. collected	5137
No. observed	3504 ($I_{obs} > 2\sigma(I)$)
R ($I_{obs} > 2\sigma(I)$)	0.0412
wR_2	0.0937
ρ_{max} (e Å^{-3})	1.42
ρ_{min} (e Å^{-3})	−1.06

Table 3
Selected bond lengths (Å) and bond angles (°) for [$Cy_3P{-}Au{-}Tu$]Cl

Bond lengths			
Au–P	2.274(2)	P–C1	1.846(9)
Au–S	2.295(2)	S–C19	1.704(9)
P–C13	1.828(10)	N1–C19	1.320(11)
P–C7	1.847(9)	N2–C19	1.310(11)
Bond angles			
P–Au–S	168.54(9)	C13–P–Au	113.0(3)
C13–P–C7	111.2(4)	C7–P–Au	106.6(3)
C13–P–C1	107.3(4)	C1–P–Au	111.8(3)
C7–P–C1	106.9(4)	C19–S–Au	110.0(3)

Table 1
Elemental analysis, m.p., IR frequencies (cm^{-1}) and % yield of [R_3PAuTu]Cl complexes

Complex	Found (Calc.) %				m.p. (°C)	ν(C=S)	% Yield
	C	H	N	S			
[Me_3PAuTu]Cl	12.7 (12.5)	3.5 (3.4)	7.4 (7.3)	8.0 (8.3)	199–200	716	63
[Et_3PAuTu]Cl [a]	19.8 (19.7)	4.6 (4.5)	6.6 (6.6)	7.2 (7.5)	135–136	718	71
[Cy_3PAuTu]Cl	38.7 (39.9)	6.4 (6.3)	5.4 (4.8)	4.8 (5.4)	204–206	690	61
[Ph_3PAuTu]Cl	40.7 (40.0)	3.3 (3.4)	5.4 (4.9)	5.7 (5.6)	146–148	710	69
[$CyPh_2PAuTu$]Cl	40.4 (39.6)	4.8 (4.4)	5.4 (4.9)	6.0 (5.6)	112–114	694	60
[$(o\text{-Tol})_3PAuTu$]Cl	43.3 (43.1)	4.5 (4.1)	4.7 (4.6)	4.6 (5.2)	199–201	712	66
[$(m\text{-Tol})_3PAuTu$]Cl	41.9 (43.1)	4.1 (4.1)	4.5 (4.6)	4.4 (5.2)	124–125	692	58

[a] Also reported earlier in Ref. [24].

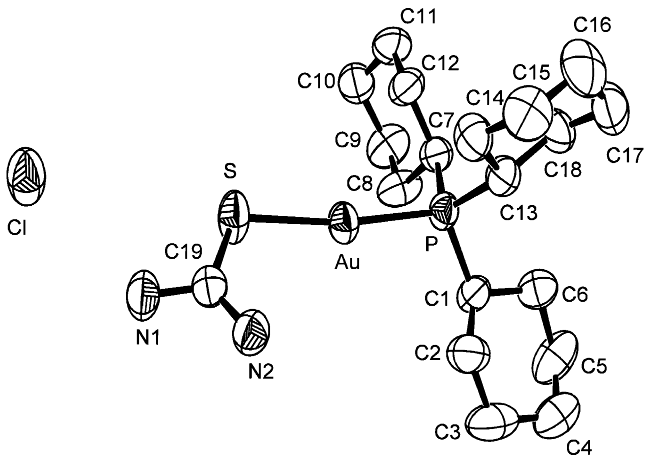

Fig. 1. ORTEP diagram of $[Cy_3PAuTu]Cl$, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

nates are deposited as supplementary materials. The drawing was prepared with ORTEP3 for windows [19,20]. The ORTEP atomic labeling scheme is given in Fig. 1.

2.4. IR and NMR measurements

The solid-state IR spectra of the complexes were recorded on a Perkin Elmer FTIR 180 spectrophotometer using KBr pellets in the 4000–400 cm^{-1} range.

The ^{31}P NMR spectra were recorded at a frequency of 202.35 MHz, using 0.269 s acquisition time, 5.00 s pulse delay and 6.20 μs pulse width (45°). The ^{31}P NMR chemical shifts were measured relative to the internal reference 85% H_3PO_4.

The ^{13}C NMR spectra were obtained at the frequency of 125.65 MHz with ^{1}H broadband decoupling at 298 K. The spectral conditions were: 32 k data points, 0.967 s acquisition time, 1.00 s pulse delay and 45° pulse angle. The ^{13}C chemical shifts were measured relative the internal reference TMS.

The ^{15}N NMR spectra were recorded at 50.55 MHz using $NH_4{}^{15}NO_3$ in D_2O as an external reference, which lies at 375.11 ppm relative to pure $MeNO_2$, 380.2 ppm [21]. The spectral conditions for ^{15}N were: 32 k data points, 0.721 s acquisition time 2.50 s delay time, 60° pulse angle and approximately 15 000 scans.

3. Results and discussion

3.1. X-ray structure description

The single crystal X-ray structure of the complex $[Cy_3PAuTu]Cl$, as a representative for the entire series, has been determined. The crystallographic data and the selected bond lengths and bond angles are given in Tables 2 and 3, respectively. The compound crystallizes in the non-centrosymmetric space group $Pna2_1$. The crystal structure, depicted in Fig. 1, shows that the geometry is not perfectly linear, with a P–Au–S bond angle of 168.54(9)°. The deviation from linearity is ascribed to the intramolecular Au···N2 contact with a distance of 3.418(3) Å. The Au–S and Au–P bond distances are 2.295(2) and 2.274(2) Å, respectively. These values are in agreement with those found in other thiourea-containing gold(I) complexes [9,10]. One nitrogen atom of thiourea (N1) is in close contact with the chloride ion with a N1···Cl distance of 3.219(3) Å, indicating $N1–H\cdots Cl^-$ hydrogen bonding. The phosphorus atom in the complex has a usual tetrahedral environment, as in the other phosphine gold(I) complexes [22,23]. The average C(Cy)–P–C(Cy) and C(Cy)–P–Au angles are 108.5 and 110.5°, respectively. The three cyclohexyl groups adopt chair conformations, similar to those found in Cy_3PAuCN and Cy_3PAuCl. A layer based molecular packing is observed, in which the rings of the neighboring molecules stack on top of each other. The shortest gold–gold distance is 8.159 Å, ruling out any metal–metal interaction.

3.2. IR studies

In the IR spectra of the complexes, the $\nu(C=S)$ mode of Tu was observed at a lower frequency compared to that for free Tu at 730 cm^{-1}. There are also strong absorptions around 1500 and 3200 cm^{-1} corresponding to $\nu(CN)$ and $\nu(NH_2)$ modes, respectively, for Tu in all complexes. The IR frequencies of the complexes are given in Table 1.

The ambidentate ligand, thiourea $\{SC(NH_2)_2\}$ is potentially capable of bonding via the sulfur or nitrogen atom [24]. A low frequency shift of the $\nu(C=S)$ absorption and a high frequency shift of the band around 3200 cm^{-1} in the gold(I) complexes indicates the existence of the thione form of Tu in the solid state.

3.3. ^{31}P NMR studies

The ^{31}P NMR spectra of the complexes were recorded in MeOD. In the ^{31}P NMR spectra of all $[R_3PAuTu]Cl$ complexes, a sharp singlet was observed for R_3P. No coupling with ^{13}C of labelled thiourea was observed in any complex. The ^{31}P NMR chemical shifts of several gold(I) complexes are given in Table 4. The ^{31}P resonance in the thiourea complexes appears downfield compared to the R_3PAuCl complexes. A downfield shift in the ^{31}P resonance of the phosphines in $[R_3PAuTu]Cl$ complexes is related to the π accepting ability of the phosphines from gold(I). The donation of electron density by Tu to gold(I) increases the back donation from gold(I) to phosphines, which would increase the double bond character of the Au–P bond resulting in a deshielding effect at the phosphorus atom. In R_3PAuCN

Table 4
^{31}P NMR chemical shifts (ppm) of various R_3PAuX complexes in MeOD

R_3P	δ $[R_3PAuCl]$	δ $[R_3PAuTu]^+$	δ $[R_3PAuCN]$ [a]
Cy_3P	54.37	58.01	53.53
Et_3P	32.81	37.90	35.35
Me_3P	−9.56	−1.86	−3.09
$(CyPh_2)P$	43.67	46.89	44.04
(*o*-Tol)$_3$P	6.29	13.75	37.38
(*p*-Tol)$_3$P	30.13	34.96 [b]	34.45
(*m*-Tol)$_3$P	32.28	37.05	35.79
Ph_3P	32.22	37.01	39.37

[a] Values taken from Ref. [11].
[b] The complex was prepared in solution.

complexes, where CN is a π acceptor ligand (with less donation of electron density to gold(I)), the ^{31}P resonance appears upfield compared to that for Tu complexes [11] (Table 4). As a result of the stronger Au–P bond in $[R_3PAuTu]Cl$ complexes, their Au–P bond lengths should be smaller compared to that in R_3PAuCN. The Au–P bond length in $[Cy_3PAuTu]Cl$ is found to be 2.274 Å, while in Cy_3PAuCN, it is 2.287 Å [23]. This difference clearly shows that $[R_3PAuTu]Cl$ type complexes have greater π character in the Au–P bond than their R_3PAuCN analogues.

3.4. ^{13}C NMR studies

The ^{13}C NMR chemical shifts for the >C=S carbon of Tu in $[R_3PAuTu]Cl$ complexes are given in Table 5 along with the values of electronic parameter, ν(CO) for the phosphines. The >C=S resonance of Tu appeared as a triplet in ^{13}C NMR due to coupling with ^{15}N with a $^{1}J(^{13}C–^{15}N)$ value of 15.7 Hz. Only small changes were observed in the coupling constant on complexation with gold(I). An upfield shift is observed in the >C=S resonance of Tu on its complexation with gold(I). The upfield shift is attributed to a lowering of >C=S bond order upon coordination and a shift of N→C electron density producing a partial double bond character in the C–N bond, as observed in the other metal complexes of thiourea [6,25]. A typical ^{13}C NMR spectrum for the $[Cy_3PAuTu]Cl$ complex is given in Fig. 2.

Table 5
^{13}C and ^{15}N NMR chemical shifts for $[R_3PAuTu]Cl$ complexes and IR wavenumbers for $R_3PNi(CO)_3$ [a] complexes

R_3P/Tu	ν (CO) in cm^{-1} of R_3P [a]	δ ^{13}C (>C=S)	δ ^{15}N
Tu		185.54	103.65
Cy_3P	2056.4	182.76	104.74
Et_3P	2061.7	180.40	106.77
Me_3P	2064.1	179.34	106.47
$(CyPh_2)P$	2064.8	177.26	
(*o*-Tol)$_3$P	2066.6	178.58	107.64
(*p*-Tol)$_3$P	2066.7	181.24 [b]	
(*m*-Tol)$_3$P	2067.9	177.33	
Ph_3P	2068.9	177.21	107.32

[a] The values are taken from Ref. [26].
[b] The complex was prepared in solution.

A correlation between the basicity of phosphines and the ^{13}C chemical shift (Table 5) is observed for $[R_3PAuTu]Cl$ complexes. The basicities or electronegativites of phosphines are measured in terms of the wavenumbers, ν(CO) for the complex, $[R_3PNi(CO)_3]$ [26]. The ν(CO) values of the phosphines are compared in Table 5. A decrease in ν(CO) is associated with a decrease in electronegativity or an increase in basicity of the phosphine.

With an increase in the electronegativity of the phosphine, the ^{13}C NMR >C=S shift difference also increases (see Table 5), e.g. the chemical shift difference between free Tu and $[Cy_3PAuTu]Cl$ is 2.78 ppm where as for $[Et_3PAuTu]Cl$, $[Me_3PAuTu]Cl$ and $[Ph_3PAuTu]Cl$ it is 5.14, 6.2 and 8.33 ppm, respectively. A similar observation is made for the coupling constants, $^{1}J(^{13}C–^{31}P)$. This shows that the Au–S bond becomes stronger as the electronegativity of the phosphine increases. Thus, the Au–S bond would be strongest when R_3P is PPh_3 while it would be weakest for the Cy_3P complex.

3.5. ^{15}N NMR studies

The ^{15}N chemical shift in all complexes were observed at a downfield position compared to that for the free ligand. The ^{15}N chemical shifts for $[R_3PAuTu]Cl$ complexes are given in Table 5. The coupling constant, $^{1}J(^{13}C–^{15}N)$ could not be resolved by ^{15}N NMR. A downfield shift in the ^{15}N resonance in all complexes demonstrates that the nitrogen of Tu is not involved in bonding to gold(I) since metal binding through nitrogen should cause an upfield shift in the ^{15}N resonance of Tu [27,28]. As discussed earlier the Au–S bond would be strongest when R_3P is PPh_3 while it would be weakest for the Cy_3P complex. This observation can also be verified by ^{15}N NMR where there is a greater shift for the more electronegative PPh_3 ligand compared to the less electronegative Cy_3P.

3.6. Conductance studies

Whether these complexes remain as two coordinates or possess a trigonal structure in solution can be established by conductivity measurements. The molar conductance for a representative complex $[Me_3PAuTu]Cl$ was measured in MeOH. The molar conductances of some compounds are given in Table 6. By comparison with the conductances of the compounds with a known number of ions, it was proved that the solution consists of two ionic species. Thus the complexes remain as two coordinates in solution.

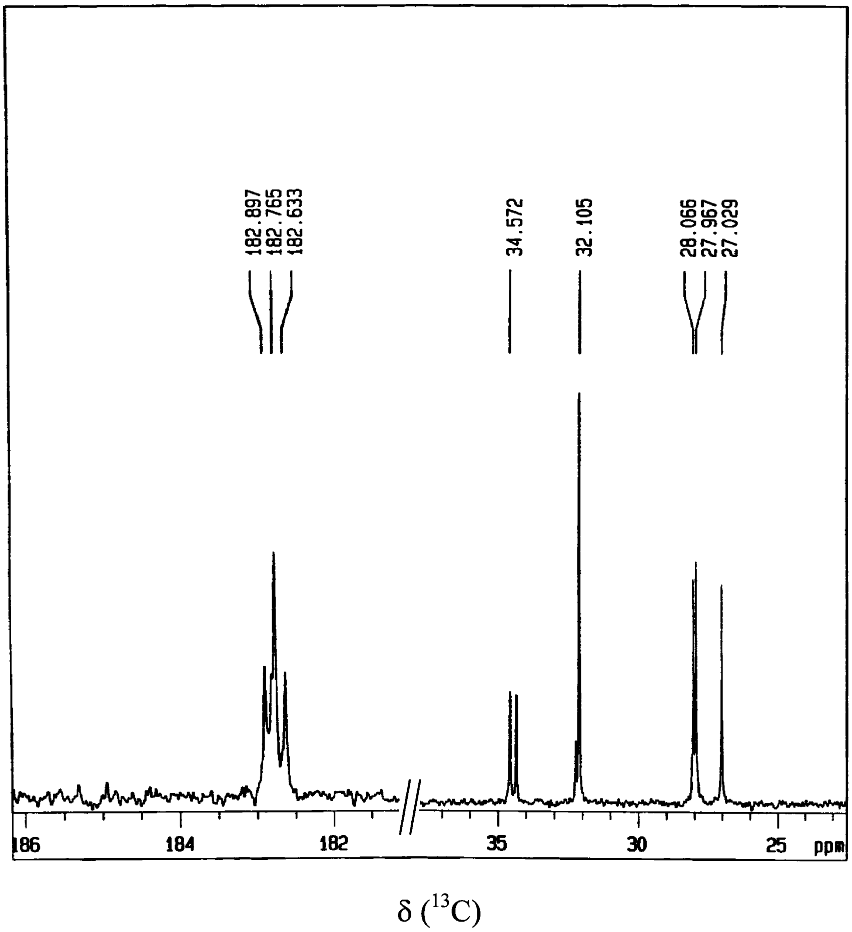

Fig. 2. The $^{13}C\{^1H\}$ NMR spectrum of $[Cy_3PAuTu]Cl$ in MeOD.

Table 6
Molar conductances and the number of ions in solution for some compounds in MeOH

Compound	Molar conductance	No. of ions in solution
$[Me_3PAuTu]Cl$	95.7	2
$[Me_3PAuCl]$	1.8	0
NH_4NO_3	86.5	2

4. Conclusions

The study provides useful information about the nature of bonding in gold(I) complexes. The chemical shifts for different complexes presented here would provide a basis for understanding and predicting the interaction of gold(I) with other phosphine and thione ligands. The X-ray results support the structures inferred from IR and NMR data.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 187414. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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