Inorganica Chimica Acta, 112 (1986) 205–208

Synthesis and Reactivity of Perchlorate Bis(tetrahydrothiophen)gold(I). ^{197}Au Mössbauer Spectra of Three-coordinate Gold(I) Complexes

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Received July 1, 1985

Abstract

The displacement of tetrahydrothiophen (tht) in $[Au(tht)_2]ClO_4$ by neutral ligands gives bi-, tri- or tetra-coordinated complexes of the type $[Au(py)_2]ClO_4$, $[(tht)AuPPh_2NHPPh_2Au(tht)](ClO_4)_2$, $[LAu(L–L)]ClO_4$ (L = tht, PPh_3; L–L = bipy, phen) or $[AuL_4]ClO_4$ (L = PPh_3, $AsPh_3$ or $SbPh_3$). The reaction between $[Au(tht)_2]ClO_4$ and $(Bu_4N)[AuR_2]$ (R = C_6F_5, C_6Cl_5, $C_6F_3H_2$) yields RAu(tht). The ^{197}Au Mössbauer spectrum of $[LAu(L–L)]ClO_4$ establishes it as a tri-coordinated species, albeit with an asymmetrically linked bidentate ligand.

Introduction

Gold(I) or gold(III) complexes containing dialkylsulphide ligands (SMe_2, tetrahydrothiopen(tht)) have frequently been used as precursors for the synthesis of new gold complexes, since they are generally stable at room temperature and their sulphide ligand can readily be replaced by other neutral or anionic groups [1–4]. In the present paper we describe the preparation of $[Au(tht)_2]ClO_4$, and report its reactions with neutral ligands or $[AuR_2]^-$ (R = C_6F_5, C_6Cl_5, $C_6F_3H_2$). These reactions produce bi-, tri- or tetra-coordinated derivatives. The ^{197}Au Mössbauer spectrum of the tricoordinated complexes has also been studied.

Experimental

The instrumentation employed and general experimental techniques were as described earlier [3]. Mössbauer measurements were made with source (Au/Pt) and absorber immersed in liquid helium as previously described [5]. The yields, melting points, C, H, N and Au analyses and conductivities of the novel complexes are listed in Table I.

Preparation of the Complexes

*$[Au(tht)_2]ClO_4$ (**I**)*

A dichloromethane (30 ml)–diethyl ether (20 ml) solution of ClAu(tht) [2] (0.320 g, 1 mmol) was added to 1 ml of a 1 M solution of tetrahydrothiophen (1 mmol) in diethyl ether, followed by an addition of $AgClO_4$ (0.207 g, 1 mmol). After 1 h stirring at room temperature, the precipitated AgCl was filtered off, and the filtrate was vacuum-concentrated to 5 ml. Addition of 20 ml of diethyl ether led to the separation of **I** as a white solid.

*$[Au(py)_2]ClO_4$ (**II**) or $[(tht)AuDPAAu(tht)](ClO_4)_2$ (**III**)*

To a solution of **I** (0.094 g, 0.2 mmol) in 20 ml of dichloromethane was added a solution of pyridine (0.1 M, 4 ml, 0.4 mmol) in ether or bis(diphenylphosphino)amine [6] (0.038 g, 0.1 mmol), and the mixture was stirred for 1 h at room temperature. The solution was vacuum-concentrated to 5 ml, and hexane was added to precipitate complexes **II** or **III**, respectively.

*BrAuDPAAuBr (**IV**)*

A mixture of **III** (0.110 g, 0.1 mmol) and $(Bu_4N)Br$ (0.065 g, 0.1 mmol) in 30 ml of dichloromethane was stirred for 1 h at room temperature. The solution was evaporated to 5 ml, and 20 ml of ether were added to precipitate a mixture of **IV** and $(Bu_4N)ClO_4$. The resulting white solid was filtered off and washed with 2 × 1 ml of ethanol, in which the ammonium salt is soluble. **IV** was recrystallized from dichloromethane/hexane.

0020-1693/86/$3.50

TABLE I. Analytical Data for Complexes I–X

Complex	Yield (%)	Melting point (°C)	Analyses (found (calc.)) (%)				Λ_M[a] (ohm^{-1} cm^2 mol^{-1})
			C	H	N	Au	
$[Au(tht)_2]ClO_4$ (**I**)	83	113(d)	20.7 (20.3)	3.5 (3.4)		41.8 (41.65)	136
$[Au(py)_2]ClO_4$ (**II**)	86	135(d)	26.05 (26.4)	2.2 (2.2)	5.9 (6.15)	43.9 (43.3)	144
$[(tht)AuDPAAu(tht)]ClO_4$ (**III**)	90	125(d)	33.65 (33.3)	3.45 (3.25)	1.65 (1.2)	33.75 (34.1)	210
BrAuDPAAuBr (**IV**)	73	175(d)	29.85 (30.75)	2.4 (2.25)	1.65 (1.5)	42.7 (41.95)	8
$(C_6F_3H_2)Au(tht)$ (**V**)	75	73(d)	28.95 (28.85)	2.35 (2.4)		47.05 (47.3)	2
$[(tht)Au(bipy)]ClO_4$ (**VI**)	88	98(d)	31.45 (31.1)	2.85 (3.0)	5.55 (5.2)	36.0 (36.4)	139
$[(tht)Au(phen)]ClO_4$ (**VII**)	94	130(d)	33.85 (34.05)	2.75 (2.85)	5.05 (4.95)	34.85 (34.85)	135
$[(Ph_3P)Au(bipy)]ClO_4$ (**VIII**)	78	127(d)	46.6 (47.05)	3.4 (3.25)	4.1 (3.9)	27.0 (27.55)	128
$[(Ph_3P)Au(phen)]ClO_4$ (**IX**)	87	207(d)	48.7 (48.75)	3.2 (3.15)	4.1 (3.8)	26.95 (26.65)	116
$[Au(SbPh_3)_4]ClO_4$ (**X**)	93	200(d)	50.8 (50.6)	3.4 (3.55)			106

[a] In acetone.

*RAu(tht) [R = C_6F_5, C_6Cl_5 or 2,4,6-$C_6F_3H_2$ (**V**)]*

To a solution of **I** (0.047 g, 0.1 mmol) in 30 ml of dichloromethane was added $(Bu_4N)[AuR_2]$ [R = C_6F_5 [2] (0.077 g, 0.1 mmol), C_6Cl_5 [2] (0.090 g, 0.1 mmol) or 2,4,6-$C_6F_3H_2$ [7] (0.072 g, 0.1 mmol)]; the mixture was stirred for 1 h at room temperature. After vacuum-evaporation to dryness, the residue was treated with 20 ml of ether. The insoluble $(Bu_4N)ClO_4$ was filtered off, and the filtrate was concentrated to 5 ml. Addition of 20 ml of hexane rendered RAu(tht) as a white solid [R = C_6F_5 (85% yield), C_6Cl_5 (89% yield) or $C_6F_3H_2$ (75% yield), respectively].

*[(tht)Au(L–L)]ClO_4 [L–L = bipy (**VI**) or phen (**VII**)]*

A mixture of **I** (0.100 g, 0.21 mmol) and 2,2′-bipyridyl (0.033 g, 0.21 mmol) or 1,10-phenanthroline (0.037 g, 0.21 mmol) in 30 ml of dichloromethane was stirred for 1 h at room temperature. Vacuum-concentration to 5 ml and addition of 20 ml of ether yielded **VI** or **VII** as yellow solids.

*[(Ph_3P)Au(L–L)]ClO_4 [L–L = bipy (**VIII**) or phen (**IX**)]*

To the yellow solution of **VI** (0.108 g, 0.2 mmol) or **VII** (0.113 g, 0.2 mmol) in 20 ml of dichloromethane was added PPh_3 (0.052 g, 0.2 mmol); the solution instantaneously turned colourless. After 1 h stirring the solution was concentrated to 5 ml. Addition of 20 ml of hexane led to the precipitation of **VIII** or **IX**, respectively.

*[AuL_4]ClO_4 [L = PPh_3, $AsPh_3$ or $SbPh_3$ (**X**)]*

To a solution of **I** (0.094 g, 0.2 mmol) in 20 ml of dichloromethane was added PPh_3 (0.262 g, 1 mmol) $AsPh_3$ (0.306 g, 1 mmol) or $SbPh_3$ (0.353 g, 1 mmol). The mixture was stirred for 1 h at room temperature and then concentrated to 5 ml. Addition of 20 ml of ether led to the precipitation of $[AuL_4]ClO_4$ [L = PPh_3 (94% yield), $AsPh_3$ (95% yield) or $SbPh_3$ (93% yield)].

Results and Discussion

The reaction of ClAu(tht) with $AgClO_4$ in the presence of tetrahydrothiophen (tht) leads to $[Au(tht)_2]ClO_4$, as represented in eqn. 1

$$ClAu(tht) + AgClO_4 + tht \longrightarrow \underset{\mathbf{I}}{[Au(tht)_2]ClO_4} + AgCl \qquad (1)$$

The resulting complex **I** is a white solid, which slowly decomposes at room temperature, but remains unchanged for months when stored at 0 °C. It is soluble in dichloromethane, chloroform and acetone (its solutions are conducting, (1:1) electrolyte), but insoluble in ether and hexane.

The tht ligand can readily be displaced by other neutral ligands, such as pyridine (py) or bis(diphenylphosphino)amine (DPA), to give mono- or bi-nuclear derivatives (eqns. 2 and 3)

$$[Au(tht)_2]ClO_4 + 2py \longrightarrow \underset{\mathbf{II}}{[Au(py)_2]ClO_4} + 2tht \qquad (2)$$

$$2[Au(tht)_2]ClO_4 + DAP \longrightarrow \underset{\mathbf{III}}{[(tht)AuDPAAu(tht)](ClO_4)_2} + 2tht \qquad (3)$$

At room temperature complexes **II** and **III** are air- and moisture-stable. Their acetone solutions are conducting with values which are characteristic for 1:1 or 1:2 electrolytes, respectively (see Table I). The tht group in complex **III** can further be displaced; thus, the reaction with $(Bu_4N)Br$ yields the neutral complex BrAuDPAAuBr (**IV**).

Taking into account that $(Bu_4N)[AuR_2]$ ($R = C_6F_5$, C_6Cl_5, $C_6F_3H_2$) reacts with $AgClO_4$ in the presence of tht to give polynuclear derivatives of the type $[AuAgR_2(tht)]_n$ [8, 9], we have studied the reaction between equimolecular amounts of $(Bu_4N)[AuR_2]$ and $[Au(tht)_2]ClO_4$. The latter process, however, takes quite a different course and yields colourless solutions containing a mixture of $(Bu_4N)ClO_4$ and RAu(tht), which can be separated by the addition of diethyl ether in which the ammonium salt is insoluble.

$$(Bu_4N)[AuR_2] + [Au(tht)_2]ClO_4 \longrightarrow 2RAu(tht) + (Bu_4N)ClO_4 \qquad (4)$$

$R = C_6F_5, C_6Cl_5, C_6F_3H_2$ (**V**)

The properties of the already known complexes with $R = C_6F_5$ and C_6Cl_5 (elemental analyses, melting points and IR spectra) coincide with the previously reported data [2, 10]. The new complex with $R = C_6F_3H_2$ is a white solid which decomposes slowly at room temperature. It is non-conducting in acetone solution, and its molecular weight determined in chloroform solution confirms its mononuclear character (392, calc. 416).

The reaction of complex **I** with bidentate ligands (L–L = bipy, phen) (1:1 molar ratio) leads to the substitution of one of the tht ligands (eqn. 5)

$$[Au(tht)_2]ClO_4 + L\text{–}L \longrightarrow [(tht)Au(L\text{–}L)]ClO_4 + tht \qquad (5)$$

L–L = bipy (**VI**), phen (**VII**)

The tht ligand in **VI** cannot be displaced by using an excess of 2,2′-bipyridyl (1:4 molar ratio), and is only partially displaced if **VII** is reacted with an excess of 1,10-phenanthroline (1:4 molar ratio), where a mixture of **VII** and $[Au(phen)_2]ClO_4$ is obtained. Nevertheless, the tht group can readily be displaced when using triphenylphosphine (eqn. 6)

TABLE II. ^{197}Au Mössbauer Data for Gold(I) Complexes

Complex	IS[a, b]	QS[b]	Line widths[b]	
$[(tht)Au(phen)]ClO_4$ (VII)	2.33	6.08	2.6	1.7
$[(Ph_3P)Au(bipy)]ClO_4$ (VIII)	3.04	6.95	2.00	2.02
$[(Ph_3P)Au(phen)]ClO_4$ (IX)	3.2	6.97	2.01	1.93
$[(Ph_3P)Au(bipy)]PF_6$	2.81	6.76[c]		
$[(Ph_3P)Au(phen)]PF_6$	2.82	7.05[c]		

[a] Relative to gold metal. [b] $mm\ s^{-1}$. [c] Ref. 8.

$$[(tht)Au(L\text{–}L)]ClO_4 + PPh_3 \longrightarrow [(Ph_3P)Au(L\text{–}L)]ClO_4 + tht \qquad (6)$$

L–L = bipy (**VIII**), phen (**IX**)

The resulting complexes are yellow (**VI** and **VII**) or white solids (**VIII** and **IX**), respectively. At room temperature **VII**–**IX** are stable, but **VI** decomposes slowly to metallic gold. They are soluble in dichloromethane, chloroform and acetone, but insoluble in ether and hexane. Their acetone solutions show conductivities characteristic for uni-univalent compounds.

Mössbauer data for complexes **VII**–**IX** are listed in Table II. The complexes containing PPh_3 (**VIII** and **IX**) show parameters which are similar to the previously reported ones for salts with PF_6^- [11] indicating a similar 'two and a half' coordination for gold, in agreement with the crystal structure reported for the cation $[(Ph_3P)Au(bipy)]^+$ [12]. The tht compound lies on a similar part of the IS–QS diagram [13], it lies close to the two-coordination region, but towards the three-coordinate complexes. This suggests that complex **VII** may also have asymmetrical coordination of the phenanthroline. The Mössbauer spectrum of **VI** could not be taken because of the low stability of this compound.

The reaction of **I** with $L = PPh_3$, $AsPh_3$ and $SbPh_3$ (1:5 molar ratio) leads to the formation of tetra-coordinated complexes (eqn. 7)

$$[Au(tht)_2]ClO_4 + 4L \longrightarrow [AuL_4]ClO_4 + 2tht \qquad (7)$$

$L = PPh_3, AsPh_3, SbPh_3$ (**X**)

The complexes with $L = PPh_3$ and $AsPh_3$ had previously been obtained by other methods [5, 14]. The complex with $L = SbPh_3$ (**X**) is a white solid which is stable at room temperature and whose acetone solution is conducting (1:1 electrolyte). The tetra-coordination of the cation had recently been confirmed [15, 16] for $[Au(SbPh_3)_4][Au(C_6F_5)_2]$.

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