

SYNTHESIS AND ^{197}Au -MÖSSBAUER SPECTROSCOPIC STUDIES OF DIHALO(PENTAFLUOROPHENYL)(BIDENTATE LIGAND)GOLD(III) COMPLEXES

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Summary

Addition of a bidentate ligand ($\text{L-L} = 1,10\text{-phenanthroline}$, $o\text{-phenylenebis(dimethylarsine)}$) to solutions of $\text{Au}(\text{C}_6\text{F}_5)_2(\text{tht})$ ($\text{X} = \text{Cl, Br}$; $\text{tht} = \text{tetrahydrothiophene}$) leads to potentially five-coordinate gold(III) derivatives. ^{197}Au Mössbauer spectroscopy points, however, to four-coordinate square-planar complexes with a weak penta-coordination in the phen-containing derivatives. The complexes react with AgClO_4 to give four-coordinate cationic complexes of the types $[\text{Au}(\text{C}_6\text{F}_5)_2\text{X}(\text{L-L})]\text{ClO}_4$ or $[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)(\text{L-L})](\text{ClO}_4)_2$.

Introduction

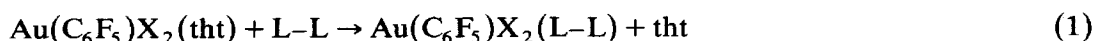
Several attempts up to the end of 1982 to prepare organogold(III) derivatives with coordination numbers higher than four were unsuccessful [1]. Even the compound $\text{R}_3\text{Au}(\text{pdma})$ ($\text{R} = \text{C}_6\text{F}_5$, $\text{pdma} = o\text{-phenylenebis(dimethylarsine)}$, a highly chelating ligand) is a four-coordinate square-planar gold(III) complex, with only one As atom of the pdma ligand bonded to gold [2]. More recently, the structure of $\text{AuCl}(\text{C}_4\text{Ph}_4)(\text{phen})$ ($\text{C}_4\text{Ph}_4 = 1,2,3,4\text{-tetraphenylbuta-1,3-diene-1,4-diyl}$, $\text{phen} = 1,10\text{-phenanthroline}$) has been elucidated [3]. In this case the gold atom can formally be described as five-coordinate, albeit with one Au-N interaction very much weaker than the other (almost $0.6 \text{ \AA}$ longer). Similar structures are observed for $\text{AuX}_3(\text{L-L})$ ($\text{X} = \text{Cl}$ or Br ; $\text{L-L} = 2,9\text{-dimethylphenanthroline}$ [4], $2\text{-(2'-pyridyl)quinoline}$ [5] or $2,2'\text{-biquinolyl}$ [6]).

In this paper we describe the synthesis of gold(III) complexes of the type $\text{Au}(\text{C}_6\text{F}_5)_2(\text{L-L})$ ($\text{X} = \text{Cl, Br}$; $\text{L-L} = \text{pdma}$ or phen). The ^{197}Au Mössbauer spectra

of some of these indicate association towards five-coordination. Moreover, cationic complexes of the types $[\text{Au}(\text{C}_6\text{F}_5)\text{X}(\text{L}-\text{L})]\text{ClO}_4$ and $[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)(\text{phen})](\text{ClO}_4)_2$ have also been prepared.

Results and discussion

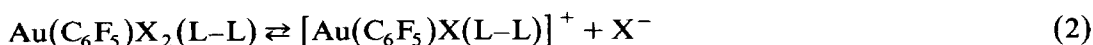
The neutral ligand (tht = tetrahydrothiophene) in $\text{Au}(\text{C}_6\text{F}_5)_2(\text{tht})$ [7] can readily be displaced by bidentate ligands, such as pdma or phen, as shown in eq. 1:



(I, L-L = phen, X = Cl; II, L-L = phen, X = Br; III, L-L = pdma; X = Cl)

The complexes I-III are yellow air- and moisture-stable solids; their molecular weights (in CHCl_3) are those expected for monomeric species (Table 1). They are either undissociated, five-coordinate species or close ion-pairs, in CHCl_3 .

Their acetone solutions are conducting, but the measured conductivities are lower than the expected for 1/1 electrolytes [8]. An equilibrium (eq. 2) is probably responsible for the observed behaviour.



In the IR spectrum, the $\nu(\text{Au}-\text{Cl})$ vibration appears at 345 cm^{-1} as a strong asymmetric band (complex I) and $\nu(\text{Au}-\text{Br})$ is observed at $240(\text{m}) \text{ cm}^{-1}$ (complex II). The corresponding band cannot be assigned for complex III owing to the presence of several absorptions due to the arsine ligand in this region.

Mössbauer data for complex I-III are listed in Table 2. Complex III is four-coordinate, the arsine acting as unidentate, as has been shown by an X-ray structure determination [2] of $\text{Au}(\text{C}_6\text{F}_5)_3(\text{dpma})$. The phen derivatives I and II have rather low IS values for their QS, especially when compared to $[\text{AuCl}_2(\text{phen})]\text{ClO}_4$. The replacement of Cl by C_6F_5 would be expected to raise both parameters. The observed decrease in IS suggests some association towards five-coordination. The values,

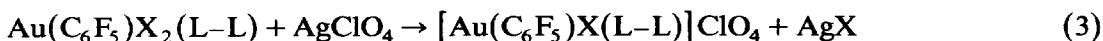
TABLE 1

ANALYTICAL DATA FOR COMPLEXES I-VII

Complex	Yield (%)	M.p. (°C)	Analyses (Found(calcd.)(%))				Λ_M ($\text{ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$)	Mol.wt. (Found (calcd.))
			C	H	N	Au		
$\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}_2(\text{phen})$ (I)	78	149(d)	35.15 (35.15)	1.3 (1.3)	4.75 (4.55)	32.4 (32.0)	34	631 (615)
$\text{Au}(\text{C}_6\text{F}_5)_2\text{Br}_2(\text{phen})$ (II)	85	245(d)	30.95 (30.7)	1.15 (1.15)	3.85 (3.95)	27.8 (27.95)	6	712 (704)
$\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}_2(\text{pdma})$ (III)	91	100	26.55 (26.65)	2.5 (2.2)	—	27.9 (27.3)	36	730 (721)
$[\text{Au}(\text{C}_6\text{F}_5)\text{Cl}(\text{phen})]\text{ClO}_4$ (IV)	66	195(d)	31.25 (31.85)	1.1 (1.2)	3.8 (4.1)	28.9 (29.0)	97	—
$[\text{Au}(\text{C}_6\text{F}_5)\text{Br}(\text{phen})]\text{ClO}_4$ (V)	86	173(d)	30.2 (29.7)	1.35 (1.11)	3.65 (3.85)	27.05 (27.2)	126	—
$[\text{Au}(\text{C}_6\text{F}_5)\text{Cl}(\text{pdma})]\text{ClO}_4$ (VI)	65	175(d)	24.45 (24.5)	2.05 (2.05)	—	24.65 (25.1)	128	—
$[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)(\text{phen})](\text{ClO}_4)_2$ (VII)	63	147(d)	42.8 (43.0)	2.2 (2.3)	2.55 (2.8)	19.5 (19.6)	208	—

however, are higher than those found [9] for $\text{AuX}_3(\text{L-L})$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{L-L} = \text{phen}$ or 2,9-dimethylphenanthroline), where the L-L ligand is asymmetrically coordinated (Au-N distances: 2.09 and 2.58 Å for the chloro and 2.08 and 2.61 Å for the bromo derivative, respectively [4]). The interaction of the second N atom with the gold centre is weaker, as has previously been found for other gold complexes (Au-N distances in $\text{AuCl}(\text{C}_6\text{H}_5)_2(\text{phen})$: 2.184 and 2.755 Å [3]).

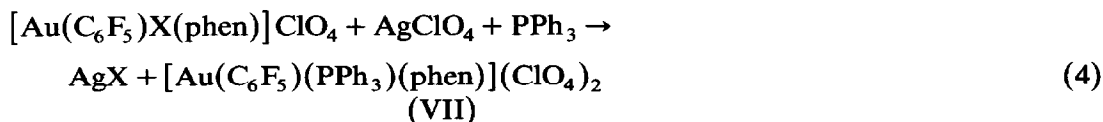
Addition of stoichiometric amounts of AgClO_4 to dichloromethane/acetone solutions of complexes I–III causes immediate precipitation of AgX .



(IV, $\text{L-L} = \text{phen}$, $\text{X} = \text{Cl}$; V, $\text{L-L} = \text{phen}$, $\text{X} = \text{Br}$; VI, $\text{L-L} = \text{pdma}$, $\text{X} = \text{Cl}$)

Removal of the AgX and evaporation of the solvent gives the corresponding complexes IV–VI. They are white, air- and moisture-stable solids, whose acetone solutions show higher conductivity than those of the starting complexes I–III, the values being those expected for 1/1 electrolytes. The vibration $\nu(\text{Au-X})$ appears at 355(m) (complex IV), or at 245(m) cm^{-1} (complex V), a little shifted towards higher energies relative to the precursors. The presence of the ClO_4^- anion is confirmed [10] by two bands at 1100(s,br) and 625(m) cm^{-1} .

Upon addition of one more mol of AgClO_4 to dichloromethane solutions of IV or V no change is observed. Addition of PPh_3 results in the precipitation of the silver halide and the white complex VII can be isolated from the filtrate (eq. 4). In acetone solution VII behaves as a (2/1) electrolyte.



Experimental

The instrumentation employed and general experimental techniques were as described earlier [11] Mössbauer measurements were made with source (Au/Pt) and

TABLE 2
GOLD-197 MÖSSBAUER DATA FOR GOLD(III) COMPLEXES

	IS ^{a,b}	QS ^b	Line widths ^b	χ^2
$\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}_2(\text{phen})$ (I)	2.92	2.33	1.86, 2.35	1.05
$\text{Au}(\text{C}_6\text{F}_5)_2\text{Br}_2(\text{phen})$ (II)	2.78	2.13	2.13, 2.00	1.18
$\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}_2(\text{pdma})$ (III)	4.09	4.94	2.28, 2.37	1.09
$[\text{AuCl}_2(\text{phen})]\text{ClO}_4$	3.01	1.95	2.06 ^c	
$\text{AuCl}_3(\text{phen})$	2.39	–	2.66	
$\text{AuCl}_3(\text{dmp})$ ^d	1.87	–	2.31	
$\text{AuBr}_3(\text{dmp})$ ^d	2.07	–	2.76	

^a Relative to gold metal. ^b mm s^{-1} . ^c Ref. 9. ^d dmp = 2,9-dimethyl-1,10-phenanthroline.

absorber immersed in liquid helium as previously described [12].

The yields, melting points, C, H, N and Au analyses, conductivities and molecular weights of the novel complexes are listed in Table 1.

Preparation of the complexes

$Au(C_6F_5)_2X_2(L-L)$ (I, $L-L = phen$; $X = Cl$; II, $L-L = phen$, $X = Br$; III, $L-L = pdma$, $X = Cl$). 1,10-phenanthroline or *o*-phenylenebis(dimethylarsine) (1 mmol) was added to a solution of $Au(C_6F_5)_2X_2(tht)$ [7] (1 mmol) in 50 ml of dichloromethane and the mixture was stirred at room temperature for 30 min. The yellow solution was concentrated to ca. 8 ml. Addition of 20 ml of hexane gave a precipitate of the yellow complexes I–III.

$[Au(C_6F_5)_2X(L-L)]ClO_4$ (IV, $L-L = phen$, $X = Cl$; V, $L-L = phen$; $X = Br$; VI, $L-L = pdma$, $X = Cl$). $AgClO_4$ (0.042 g, 0.2 mmol) was added to a solution of I, II or III (0.2 mmol) in a mixture of 25 ml of dichloromethane and 5 ml of acetone. After 5 h stirring at room temperature the precipitated AgX was filtered off and the filtrate was concentrated to ca. 5 ml. Addition of 20 ml of hexane gave a precipitate of complexes IV–VI.

$[Au(C_6F_5)_2(PPh_3)(phen)](ClO_4)_2$ (VII). $AgClO_4$ (0.042 g, 0.2 mmol) was added to a solution of IV (0.115 g, 0.2 mmol) in a mixture of 30 ml of dichloromethane and 5 ml of acetone. No precipitate of $AgCl$ was produced by 3 h stirring at room temperature. PPh_3 (0.053 g, 0.2 mmol) was added and the stirring was continued for 1 h. The precipitated $AgCl$ was filtered off and the filtrate was reduced to ca. 5 ml. Addition of 20 ml of hexane led to precipitation of the white VII.

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