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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 (L–L = 1,10-phenanthroline, *o*-phenylenebis(dimethylarsine)) to solutions of $Au(C_6F_5)X_2(tht)$ ($X = Cl$, Br; tht = 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 $[Au(C_6F_5)X(L–L)]ClO_4$ or $[Au(C_6F_5)(PPh_3)(L–L)](ClO_4)_2$.

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 $R_3Au(pdma)$ ($R = C_6F_5$, pdma = *o*-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 $AuCl(C_4Ph_4)(phen)$ (C_4Ph_4 = 1,2,3,4-tetraphenylbuta-1,3-diene-1,4-diyl, phen = 1,10-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 Å longer). Similar structures are observed for AuX_3(L–L) ($X = Cl$ or Br; L–L = 2,9-dimethylphenanthroline [4], 2-(2′-pyridyl)quinoline [5] or 2,2′-biquinolyl [6]).

In this paper we describe the synthesis of gold(III) complexes of the type $Au(C_6F_5)X_2$(L–L) ($X = Cl$, Br; L–L = pdma or phen). The ^{197}Au Mössbauer spectra

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of some of these indicate association towards five-coordination. Moreover, cationic complexes of the types $[Au(C_6F_5)X(L{-}L)]ClO_4$ and $[Au(C_6F_5)(PPh_3)(phen)](ClO_4)_2$ have also been prepared.

Results and discussion

The neutral ligand (tht = tetrahydrothiophene) in $Au(C_6F_5)X_2(tht)$ [7] can readily be displaced by bidentate ligands, such as pdma or phen, as shown in eq. 1:

$$Au(C_6F_5)X_2(tht) + L{-}L \rightarrow Au(C_6F_5)X_2(L{-}L) + tht \qquad (1)$$

(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.

$$Au(C_6F_5)X_2(L{-}L) \rightleftarrows [Au(C_6F_5)X(L{-}L)]^+ + X^- \qquad (2)$$

In the IR spectrum, the ν(Au–Cl) vibration appears at 345 cm^{-1} as a strong asymmetric band (complex I) and ν(Au–Br) is observed at 240(m) 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 $Au(C_6F_5)_3(dpma)$. The phen derivatives I and II have rather low IS values for their QS, especially when compared to $[AuCl_2(phen)]ClO_4$. 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 (ohm^{-1}cm^2 mol^{-1})	Mol.wt. (Found (calcd.))
			C	H	N	Au		
$Au(C_6F_5)Cl_2(phen)$	78	149(d)	35.15	1.3	4.75	32.4	34	631
(I)			(35.15)	(1.3)	(4.55)	(32.0)		(615)
$Au(C_6F_5)Br_2(phen)$	85	245(d)	30.95	1.15	3.85	27.8	6	712
(II)			(30.7)	(1.15)	(3.95)	(27.95)		(704)
$Au(C_6F_5)Cl_2(pdma)$	91	100	26.55	2.5	–	27.9	36	730
(III)			(26.65)	(2.2)		(27.3)		(721)
$[Au(C_6F_5)Cl(phen)]ClO_4$	66	195(d)	31.25	1.1	3.8	28.9	97	–
(IV)			(31.85)	(1.2)	(4.1)	(29.0)		
$[Au(C_6F_5)Br(phen)]ClO_4$	86	173(d)	30.2	1.35	3.65	27.05	126	–
(V)			(29.7)	(1.11)	(3.85)	(27.2)		
$[Au(C_6F_5)Cl(pdma)]ClO_4$	65	175(d)	24.45	2.05	–	24.65	128	–
(VI)			(24.5)	(2.05)		(25.1)		
$[Au(C_6F_5)(PPh_3)(phen)][ClO_4]_2$	63	147(d)	42.8	2.2	2.55	19.5	208	–
(VII)			(43.0)	(2.3)	(2.8)	(19.6)		

however, are higher than those found [9] for $AuX_3(L-L)$ ($X = Cl,Br$; $L-L$ = 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 $AuCl(C_4Ph_4)(phen)$: 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.

$$Au(C_6F_5)X_2(L-L) + AgClO_4 \rightarrow [Au(C_6F_5)X(L-L)]ClO_4 + AgX \qquad (3)$$

(IV, L–L = phen, X = Cl; V, L–L = phen, X = Br; VI, L–L = pdma, X = 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 ν(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.

$$[Au(C_6F_5)X(phen)]ClO_4 + AgClO_4 + PPh_3 \rightarrow$$
$$AgX + \underset{(VII)}{[Au(C_6F_5)(PPh_3)(phen)](ClO_4)_2} \qquad (4)$$

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
$Au(C_6F_5)Cl_2(phen)$ (I)	2.92	2.33	1.86, 2.35	1.05
$Au(C_6F_5)Br_2(phen)$ (II)	2.78	2.13	2.13, 2.00	1.18
$Au(C_6F_5)Cl_2(pdma)$ (III)	4.09	4.94	2.28, 2.37	1.09
$[AuCl_2(phen)]ClO_4$	3.01	1.95	2.06 [c]	
$AuCl_3(phen)$	2.39	–	2.66	
$AuCl_3(dmp)$ [d]	1.87	–	2.31	
$AuBr_3(dmp)$ [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

$Au(C_6F_5)X_2(L–L)$ (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 $Au(C_6F_5)X_2(tht)$ [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.

$[Au(C_6F_5)X(L–L)]ClO_4$ (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.

$[Au(C_6F_5)(PPh_3)(phen)](ClO_4)_2$ (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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