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GOLD(III) COMPLEXES CONTAINING 2-[(PHENYLAZO)PHENYL] AS A CHELATING LIGAND

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Summary

The complex [Au(Az)Cl_2] (Az = 2-(phenylazo)phenyl, 2-(C_6H_4N=NC_6H_5)) reacts with AgAc (Ac = CH_3COO) to give [Au(Az)(Ac)$_2$]. Treatment of this complex with acids such as H_2ox (ox = OOC–COO), HCl or (pyH)ClO_4 (pyH = pyridinium) in 1/1 molar ratio has given [Au(Az)(ox), [Au(Az)(Ac)Cl] and [Au(Az)(Ac)(py)]ClO_4. [Au(Az)(py)$_2$](ClO_4)$_2$ can be prepared by treating (i) [Au(Az)(Ac)$_2$] with (pyH)ClO_4 (1/2), (ii) [Au(Az)(Ac)(py)]ClO_4 with (pyH)ClO_4 (1/1), or (iii) [Au(Az)Cl_2] with pyridine in the presence of $NaClO_4$. It is possible to substitute one or both pyridine ligands of [Au(Az)(py)$_2$](ClO_4)$_2$ to give the ions [Au(Az)(py)($AsPh_3$)]$^{2+}$, [Au(Az)(bipy)]$^{2+}$ and [Au(Az)(quinO)]$^+$ (quinOH = 8-hydroxyquinoline).

Introduction

We previously described [1] the synthesis of [Au(Az)Cl_2] (Az = 2-(phenylazo)phenyl, 2-(C_6H_4N=NC_6H_5) by a transmetallation reaction between [Hg(Az)Cl] and [$AuCl_3$(tht)] (tht = tetrahydrothiophene). The [Au(Az)Cl_2] reacts with neutral ligands to give complexes of the types [Au(Az)Cl_2L] and [Au(Az)ClL_2]$^+$ by cleavage of the N → Au bond [2]. On the other hand, we found that the related complex [Au(Bz)Cl_2] (Bz = 2-$C_6H_4CH_2NMe_2$) reacts with various neutral ligands (even in excess) to give [Au(Bz)ClL]$^+$ complexes in which the chelate structure is maintained [3].

In this paper we describe the preparation of neutral and cationic chelate 2-[(phenylazo)phenyl]gold(III) complexes, the first such cationic species to be described.

Results and discussion

When [Au(Az)Cl_2] and AgAc (Ac = CH_3COO) react in acetone (1/2), AgCl is precipitated and a solution of [Au(Az)(Ac)$_2$] (I) is obtained. The solution of I in acetone reacts with H_2ox (ox = OOC–COO), HCl or (pyH)ClO_4 (1/1) to give [Au(Az)(ox)] (II), [Au(Az)(Ac)Cl] (III) or [Au(Az)(Ac)(py)] ClO_4 (IV) respectively.

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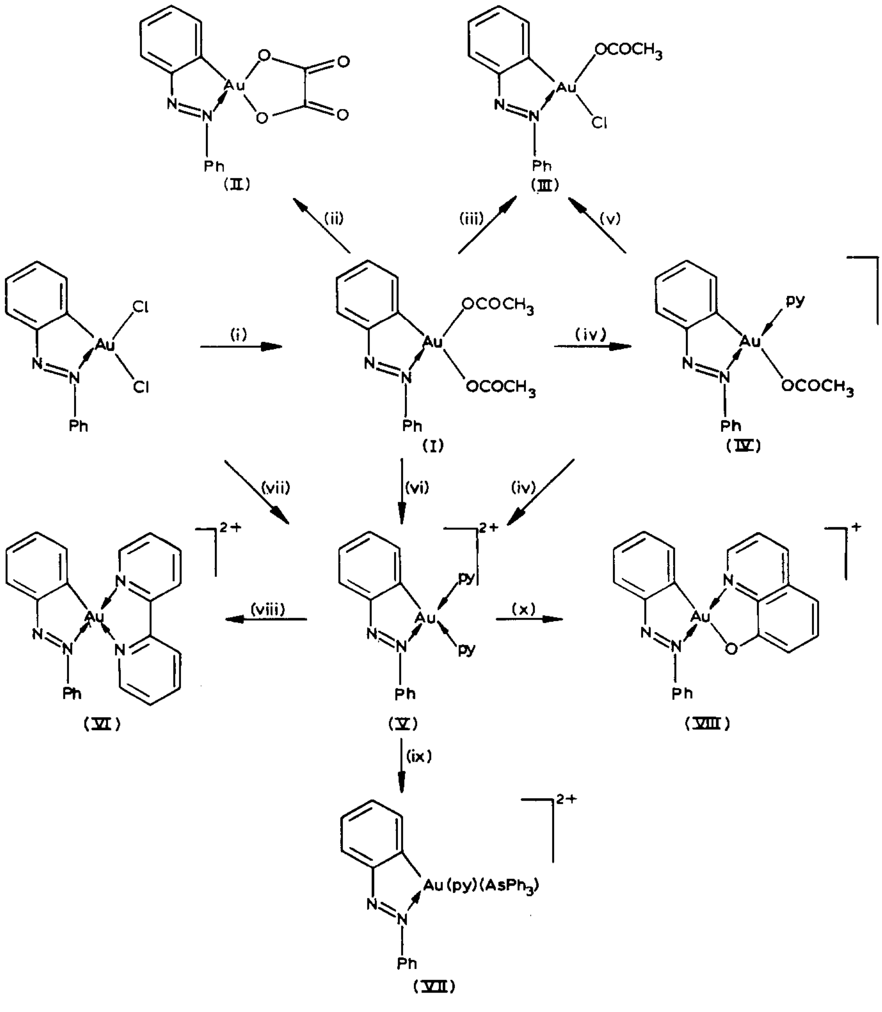
TABLE 1

ANALYTICAL AND OTHER DATA FOR COMPLEXES I–VIII

Complex [a]	M.P. (°C)	Colour	Λ_M [b]	Analytical data (Found (calcd.) (%))				Yield (%)
				C	H	N	Au	
$[Au(Az)(Ac)_2]$ (I)	140 (dec.)	yellow	1,5	38.78 (38.72)	2.76 (3.05)	5.33 (5.64)	40.03 (39.69)	75
$[Au(Az)(ox)]$ (II)	129 (dec.)	brown	1	35.44 (36.07)	2.16 (1.95)	6.18 (6.01)	41.37 (42.25)	76
$[Au(Az)(Ac)Cl]$ (III)	170 (dec.)	yellow	0	35.80 (35.57)	2.80 (2.56)	6.17 (5.93)	41.26 (41.67)	90
$[Au(Az)(Ac)(py)]ClO_4$ (IV)	112 (dec.)	yellow	109	36.41 (37.06)	3.15 (2.78)	6.82 (6.82)	31.55 (31.98)	94
$[Au(Az)(py)_2](ClO_4)_2$ (V)	210 (dec.)	yellow	180	35.49 (35.94)	2.93 (2.60)	7.28 (7.62)	26.31 (26.79)	97
$[Au(Az)(bipy)](ClO_4)_2$ (VI)	140 (dec.)	orange	185	36.54 (36.04)	2.68 (2.34)	7.54 (7.64)	26.34 (26.86)	93
$[Au(Az)(py)(AsPh_3)](ClO_4)_2$ (VII)	110	orange	157	43.46 (43.68)	3.21 (3.04)	4.07 (4.36)	19.93 (20.46)	75
$[Au(Az)(quinO)]ClO_4$ (VIII)	120 (dec.)	brown-red	98	40.41 (40.56)	2.30 (2.43)	7.12 (6.76)	31.14 (31.68)	61

[a] Az = 2-$(C_6H_4N{=}NC_6H_5)$. [b] On approx. 10^{-4} M solution in acetone (ohm^{-1} cm^2 mol^{-1}).

III cannot be prepared by treating [Au(Az)Cl$_2$] with AgAc (1/1) because in this case a mixture of [Au(Az)Cl$_2$] and I is obtained. The reaction between I and (pyH)ClO$_4$ in the molar ratio 1/2 gives the dicationic complex [Au(Az)(py)$_2$](ClO$_4$)$_2$ (V); the same method has been used to prepare [Au(Bz)(py)$_2$]$^{2+}$ [4]. Complex V can also be obtained by treating IV with (pyH)ClO$_4$ (1/1) or [Au(Az)Cl$_2$] with pyridine and NaClO$_4$, both in excess. [Au(Az)Cl$_2$] reacts with pyridine to give a mixture of the starting complex and, probably, [Au(Az)Cl$_2$(py)]; when the mixture was recrystallized only [Au(Az)Cl$_2$] was isolated [2]. We suggested that the process is likely to involve an equilibrium which lies over to the left, because of the poor donor ability of the ligand and the low solubility of [Au(Az)Cl$_2$]. However, if the reaction is



SCHEME 1. For all the cationic complexes the counter anion is ClO$_4^-$. (i) +2AgAc, −2AgCl; (ii) +H$_2$ox, −2HAc; (iii) +HCl, −HAc; (iv) +(pyH)ClO$_4$, −HAc; (v) +HCl, −(pyH)ClO$_4$; (vi) +2(pyH)ClO$_4$, −2HAc; (vii) +2py+2NaClO$_4$·H$_2$O, −2NaCl; (viii) +bipy, −2py; (ix) +AsPh$_3$, −py; (x) +quinOH, −(pyH)ClO$_4$, −py.

carried out in the presence of $NaClO_4$ the two chloride ligands are replaced by pyridine and complex V is obtained.

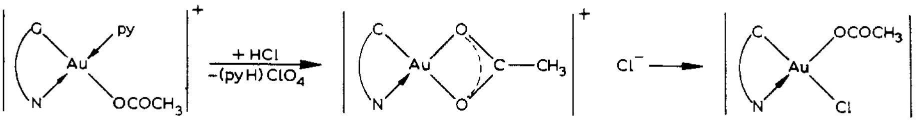
In an attempt to prepare $[Au(Az)Cl(py)]ClO_4$ we treated $[Au(Az)(Ac)(py)]ClO_4$ (IV) with HCl (1/1), but substitution of the pyridine ligand occurred to give complex III.

The reactions between $[Au(Az)(py)_2](ClO_4)_2$ (V) and 2,2'-bipyridine (bipy), or $AsPh_3$, or 8-hidroxyquinoline (quinOH) (1/1) give $[Au(Az)(bipy)](ClO_4)_2$ (VI), $[Au(Az)(py)(AsPh_3)]ClO_4)_2$ (VII) or $[Au(Az)(quinO)]ClO_4$ (VIII), respectively. The reactions are summarized in Scheme 1. Complex VI cannot be prepared by treating $[Au(Az)Cl_2]$ with bipy and $NaClO_4$ (1/1/3); this procedure leads to the previously reported $[Au(Az)Cl(bipy)]ClO_4$ [5].

Several attempts to prepare PPh_3 complexes, by treating I and $(HPPh_3)ClO_4$ (1/1 or 1/2) or V with PPh_3 (1/1, 1/2 or 1/3), always gave complex mixtures which we could not separate. When V was the starting material the mixtures always contained coordinated pyridine (IR). Similarly, V reacts with $AsPh_3$ (1/2) to give only the mono-substituted complex VII. $[Au(Az)Cl_2]$ reacts [2] with $AsPh_3$ to give $[Au(Az)Cl_2(AsPh_3)]$ by cleavage of the N → Au bond. It is possible that the dicationic nature of V strengthens both the azo N → Au and py → Au bonds.

The complexes show conductivities in acetone and elemental analysis consistent with their formulae (see Table 1).

The IR spectrum of [Au(Az)(Ac)Cl] (III) shows a strong band at 300 cm^{-1} that must be assigned to $\nu(AuCl)$ *trans* to the phenyl group [1,2,6]. It also shows two strong bands at 1665 and 1360 cm^{-1} corresponding to $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO)_2$ of a monocoordinate acetato ligand [7]. Complex I shows two pairs of strong bands, one at 1665, 1629, and the other at 1360, 1310 cm^{-1} as observed for the related complex $[Au(Bz)(Ac)_2]$ [3]. By comparing these frequencies with those observed in III a tentative assignment of $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ of the acetato ligand *trans* to the nitrogen atom of the azo group (1665, 1360 cm^{-1}) and *trans* to the phenyl group (1629, 1310 cm^{-1}) can be made. On the basis of this assignment complex IV must have the acetato ligand *trans* to the phenyl group because it shows $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ at 1620 and 1300 cm^{-1}, respectively. The other reported [2] cationic 2-[(phenylazo)phenyl]gold(III) complexes, $[Au(Az)Cl(L)_2]$, also have the anionic ligands (phenyl and chloro) mutually *trans*. Assuming such a geometry for IV, its reaction with HCl must take place with isomerization to give III. It is possible that such a process occurs through a chelated acetato complex.



(IV) (III)

The IR spectrum of the oxalato complex II shows two strong bands at 1735 and 1680 cm^{-1}. Its monomeric nature in chloroform solution (1.27×10^{-2} *M*) was established by osmometry (found, 442; calculated 466).

We tentatively assign to VIII the structure shown in Scheme 1 on the basis of (i) the crystal structure of the related $[Au(Bz)(quinO)]^+$ complex [8], and (ii) the above-mentioned tendency of this type of complex to have the anionic ligands *trans* to the phenyl group.

Experimental

IR spectra were recorded on a Perkin–Elmer 1430 spectrophotometer. Conductivities were measured in acetone (5×10^{-4} M) solutions with a Philips 9501 conductimeter. Molecular weight of II was determined with a Knauer osmometer. Melting points were determined on a Reichert apparatus and are uncorrected. C, H, and N analyses were carried out with a Perkin–Elmer 240 C microanalyzer. Au was determined by ashing the samples with an aqueous solution of hydrazine. Solvents were distilled before use. All the reactions were carried out at room temperature with magnetic stirring and without special precautions to exclude moisture. $[Au(Az)Cl_2]$ was prepared as reported [1,2]. $(pyH)ClO_4$ was prepared from the reaction of equimolar amounts of pyridine and $HClO_4$ in diethyl ether. Details given below refer in each case to the method giving the highest yield.

$[Au(Az)(Ac)_2]$ (I). Solid AgAc (53 mg, 0.32 mmol) was added to a suspension of $[Au(Az)Cl_2]$ (72 mg, 0.16 mmol) in acetone (5 ml). The suspension was stirred for 30 min in the dark and then concentrated to dryness. The residue was extracted with dichloromethane (3 × 5 ml), the AgCl was filtered off, and the solution concentrated (1 ml). Addition of diethyl ether (10 ml) led to precipitation of I as a yellow solid, which was filtered off, and recrystallized from dichloromethane/diethyl ether.

$[Au(Az)(ox)]$ (II). Solid oxalic acid (11 mg, 0.12 mmol) was added to a suspension of I (60 mg, 0.12 mmol) in acetone (5 ml). After 15 h stirring the solution was concentrated (1 ml) and n-hexane was added (10 ml) to precipitate II as a brown solid. This was recrystallized from dichloromethane/diethyl ether.

$[Au(Az)(Ac)Cl]$ (III). An aqueous solution of HCl (2.4 ml, 0.03 M, 0.07 mmol) was added to a solution of I (34.5 mg, 0.07 mmol) in acetone (18 ml). The solution was stirred for 4 h and then concentrated (5 ml). Addition of diethyl ether (15 ml) precipitated III as a yellow solid, which was recrystallized from acetone/diethyl ether.

$[Au(Az)(Ac)(py)](ClO_4)$ (IV). Solid $(pyH)ClO_4$ (18 mg, 0.1 mmol) was added to a solution of I (50 mg, 0.1 mmol) in dichloromethane (10 ml). The solution was stirred for 1 h and then concentrated (1 ml). Addition of diethyl ether (10 ml) precipitated IV as a yellow solid which was recrystallized from dichloromethane/diethyl ether.

$[Au(Az)(py)_2](ClO_4)_2$ (V). Solid $NaClO_4 \cdot H_2O$ (38 mg, 0.27 mmol) and pyridine (0.1 ml, 1.2 mmol) were added to a suspension of $[Au(Az)Cl_2]$ (43 mg, 0.09 mmol) in acetone (5 ml). The suspension was stirred for 1 h then concentrated to dryness. The residue was extracted with dichloromethane (3 × 3 ml), the extract was filtered, and the filtrate concentrated (1 ml). Diethyl ether was added (10 ml) to precipitate V as a yellow solid, which was recrystallized from dichloromethane/diethyl ether.

$[Au(Az)(bipy)](ClO_4)_2$ (VI). Solid 2,2′-bipyridine (5.8 mg, 0.05 mmol) was added to a solution of V (40 mg, 0.05 mmol) in dichloromethane (6 ml). The solution was stirred for 5 h then concentrated (3 ml). Addition of diethyl ether (15 ml) precipitated VI as an orange solid, which was recrystallized from dichloromethane/diethyl ether.

$[Au(Az)(py)(AsPh_3)](ClO_4)_2$ (VII). Solid $AsPh_3$ (14.7 mg, 0.05 mmol) was added to a solution of V (35.4 mg, 0.05 mmol) in dichloromethane (5 ml). The solution was stirred for 30 min then concentrated (3 ml). Addition of diethyl ether (10 ml) precipitated VII as an orange solid, which was recrystallized from dichloromethane/diethyl ether.

[Au(Az)(quinO)]ClO$_4$ (VIII). Solid 8-hydroxyquinoline (22.3 mg, 0.15 mmol) was added to a solution of V (113 mg, 0.15 mmol) in dichloromethane (5 ml). The suspension was stirred for 20 min and then (pyH)ClO$_4$ filtered off. The solution was concentrated (1 ml), and addition of diethyl ether (10 ml) precipitated VIII as a brown-red solid, which was recrystallized from dichloromethane/diethyl ether.

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