Inorganica Chimica Acta, 99 (1985) 165–168

Some Gold(III) Derivatives of Pyrazoles

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Received July 27, 1984

Abstract

Various gold(III) derivatives of pyrazoles, pzH, were obtained and characterized. Besides the salt $[3,5\text{-}Ph_2pzH_2][AuCl_4]$, they included adducts, $AuCl_3 \cdot pzH$, μ-pyrazolato-N,N'-derivatives, $[Cl_2Au(pz)]_n$ (such as: n = 2 and pz = 3,5-diphenyl-4-chloropyrazolato), and one derivative containing both a neutral pyrazole and a pyrazolato ligand, $Cl_2Au(3,5\text{-}Ph_2pz\text{-}N)(3,5\text{-}Ph_2pzH)$.

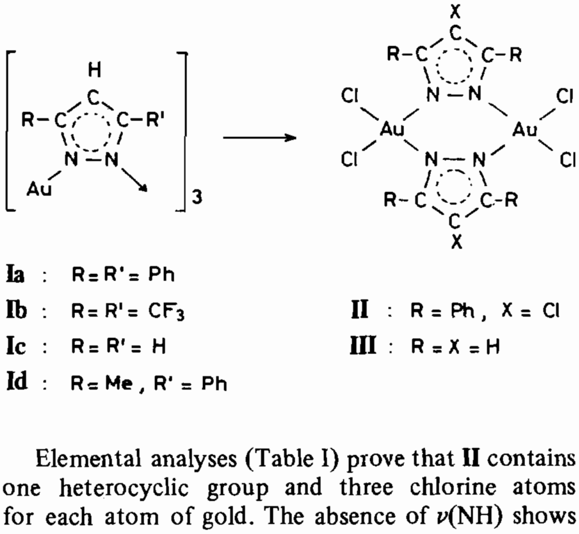
Introduction

The interaction of gold(I) with pyrazoles* has been widely explored, and a variety of derivatives containing neutral pyrazoles, pzH, or pyrazolato anions, pz^-, have been described. Depending on the substituents of the heteroaromatic ring, and on the co-ligand, mono-, bi-, and trinuclear species such as: $(pzH)_nAuCl$ [1], $[(Ph_3P)Au(3,5\text{-}Me_2pzH)]BF_4$ [2], $R_3PAu(pz\text{-}N)$ [3, 4], $\{[(Ph_3P)Au]_2(\mu\text{-}[3,5\text{-}Me_2pz\text{-}N,N'])\}BF_4$ or various $Au_3(\mu\text{-}[pz\text{-}N,N'])_3$ [3–5] have been isolated. With gold(III), the other common oxidation state of this element, the chemistry of these ligands is very limited, only two $AuCl_3 \cdot pzH$ compounds being known, where pzH is 3(5)-MepzH or $3,5\text{-}Me_2pzH$ [6]; they were obtained by pouring an aqueous solution of the ligand into an aqueous solution of chloroauric acid [6].

Following our observation that $(\mu\text{-}[3,5\text{-}Ph_2pz\text{-}N,N'])_3Au_3$ reacts with *aqua regia* yielding a gold(III) derivative, we investigated the interaction of pyrazoles with gold(III) and here we report some gold(III) derivatives containing pyrazole, pyrazolato, or both ligands.

Results and Discussion

Treatment of $(3,5\text{-}Ph_2pz)_3Au_3$, **Ia**, with *aqua regia* affords a stable yellow-orange compound **II**, according to the following reaction:



Ia : R = R' = Ph
Ib : R = R' = CF_3
Ic : R = R' = H
Id : R = Me, R' = Ph

II : R = Ph, X = Cl
III : R = X = H

Elemental analyses (Table I) prove that **II** contains one heterocyclic group and three chlorine atoms for each atom of gold. The absence of ν(NH) shows that the diazole ring has not undergone protonation, and rules out the presence of neutral pyrazole (for example $AuCl_3 \cdot pzH$, *cf.* [6]). Besides, no ν(CH) is now observed above 3100 cm^{-1}, that is, in the region which is characteristic of the heteroaromatic rings,

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*Pyrazole, $C_3H_4N_2$, is indicated by PzH, while pzH means a pyrazole, with or without substituents. If these are present they are indicated as follows: $3,5\text{-}Ph_2pzH$ means 3,5-diphenylpyrazole.

0020-1693/85/$3.30

TABLE I. Analytical and Other Data.

Compound	Analytical data[a]				Conductance data[b]	
	C	H	N	other	Λ[c]	conc.[d]
$[AuCl_2(3,5\text{-}Ph_2\text{-}4\text{-}Cl\text{-}pz)]_2$ **II**	34.96	2.05	5.29	1050[e]	f	0.3
	34.47	1.92	5.38	1043 M.W.		
$[AuCl_2(Pz)]_n$ **III**	11.33	1.00	8.50	20.88	2.5	0.2
	10.75	0.90	8.36	21.2 (Cl)		
$AuCl_3(3,5\text{-}Me,Ph\text{-}pzH)$ **IV**	25.88	2.05	6.37	478		
	26.02	2.18	6.07	461 M.W.		
$[AuCl_2(3,5\text{-}Me,Ph\text{-}pz)]_2$ **V**	28.30	2.10	6.60	896	f	0.61
	28.25	2.13	6.59	850 M.W.		
$AuCl_3 \cdot PzH$ **VI**	10.13	1.37	7.35		3.9	0.58
	9.70	1.08	7.54		94.6	0.46[g]
$AuCl_2(3,5\text{-}Ph_2pz)(3,5\text{-}Ph_2pzH)$ **VII**	62.58	4.59	9.46	6.34	2.7	0.15
	62.71	4.10	9.75	6.18 (Cl)		
$[3,5\text{-}Ph_2pzH_2][AuCl_4]$ **VIII**	46.13	3.80	7.29	19.0	15.7	0.22
	46.18	3.07	7.18	18.2 (Cl)		

[a] Found/calculated (%). [b] CH_2Cl_2 solution, room temperature. [c] ohm^{-1} cm^2 mol^{-1}. [d] $\times 10^{-3}$ molar. [e] Osmometry in chloroform. Additional data: Au, 37.5; Cl, 20.3%. Calculated: Au, 37.77; Cl, 20.42%. [f] Too low to be measured. [g] Acetone solution.

TABLE II. Au–Cl Stretching Vibration *trans* to L ligand in Various Gold(III) Species.

Species	(Au–Cl) (cm^{-1})	ref.
$[PhAuCl_3]^-$	289	7
Ph_3PAuCl_3	312	8
Me_2SAuCl_3	313	9
$(pyridine)AuCl_3$	333	8, 10
$(diazepine)AuCl_3$	340	11
$[(dipy)AuCl_2]^+$	360	12
$[AuCl_4]^-$	361	13
$[Cl_2Au(\mu\text{-}pz\text{-}N,N')]_2$	367	this work

thus suggesting that no hydrogen is present on the 4-position of the pyrazole. Independently, the proton NMR spectrum supports the absence of a hydrogen atom in the 4-position. Finally, a molecular weight determination in chloroform solution indicates a binuclear species. The combined evidence suggests that in the compound **II** there are 4-chlorinated pirazolato bridges in a six-membered cycle containing two Au(III) nuclei in the usual four-coordinate arrangement. It seems then that the isolation of **II** in the strongly acid and oxidizing conditions used is possible, thanks to the stability of this hexaatomic ring; on the other hand the enneaatomic ring present in **I** was found to be resistant to acid, bases, or oxidizing agents such as iodine [3].

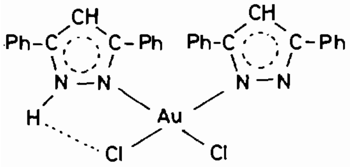
The infrared spectrum of **II** shows a gold-chlorine stretching frequency at 367 cm^{-1}, a value to be compared with the infrared-active stretching vibration observed in the anion $[AuCl_4]^-$ and in the $(dipy)AuCl_2^+$ cation (see Table II). It seems that the ν(Au–Cl) vibration of our compound lies in the upper part of the range of values of the Table II; consequently, a low *trans*-influence has to be assumed for the 3,5-Ph_2-4-Cl-pyrazolate ligand. Independently, in other cases the *trans*-influence of the pyrazolato ligand was found to be low, moderately affected by substituents, and of the same order of magnitude as that of the chloride. This was established on the basis of infrared, NMR, and X-ray crystal structure determinations for the same metal in a different oxidation state or for a different metal, *e.g.*: $[(Ph_3P)Au(3,5\text{-}Me_2pzH)]BF_4$ [2], $[Ph_2P(CH_2)_nPPh_2]Pt(pz\text{-}N)_2$, or $\{[Ph_2P(CH_2)_nPPh_2]Pt(pzH)_2\}[BF_4]_2$ [14].

The $\overline{\mathrm{Au{-}N{-}N{-}Au{-}N{-}N}}$ ring present in **II** will probably be in the typical boat configuration, already established through X-ray crystal structure determination in other dinuclear pyrazolates where the metal atoms lie in a square planar surrounding, *e.g.* $[Rh(Pz)(CO)P(OPh)_3]_2$ and $[Rh(3,5\text{-}Me_2pz)(CS)(PPh_3)]_2$ [15].

The reaction was extended to several other $Au_3(pz)_3$ species with various results which underline the sensitivity of metal derivatives of pyrazole to ring substitution. Indeed, **Ib**, $Au_3[3,5\text{-}(CF_3)_2pz]_3$, is unaffected by the treatment with *aqua regia* for three days, in line with its stability, while the corresponding derivative of the unsubstituted pyrazole, **Ic**, is only oxidized (but is not chlorinated on the ring) to give the sparingly soluble compound $[Cl_2Au(Pz)]_n$,

III, where n is likely to be two by analogy with **II** and with **V**. Owing to extensive decomposition no product is isolated after similar treatment of **Id**, although the product expected, namely [Cl$_2$-Au(3,5-Me,Phpz)]$_2$, **V**, is isolated when the adduct between Au$_2$Cl$_6$ and the corresponding pyrazole, **IV**, is reacted in the presence of potassium hydroxide. One of the possible intermediates, the adduct AuCl$_3$·pzH, is isolated when the said pyrazole or the unsubstituted pyrazole are reacted with Au$_2$Cl$_6$, affording the sparingly soluble compound AuCl$_3$-(3,5-Me,Ph-pzH), **IV**, or AuCl$_3$·PzH, **VI**, in which the gold(III) atom is likely to lie in the usual square planar arrangement. Both **IV** and **VI** show the required ν(N–H), ν(C–H), and ν(Au–Cl) stretching vibrations in the infrared spectrum.

Also, the reaction of gold(III) chloride with pyrazole seems to be rather sensitive to the presence of substituents on the heterocyclic ligand, as shown by the results obtained when 3,5-Ph$_2$pzH is reacted in the place of another pyrazole. In this case the main product is Cl$_2$Au(pz-N)(pzH), **VII** (orange), where the usual square planar Au(III) and hydrogen-bonding are likely to be present, *e.g.* as in



Two gold–chlorine stretching vibrations are found, at 371 and 360 cm^{-1}, while in the N–H stretching region there is a broad absorption from 3200 to 2400 cm^{-1}. The formation of **VII** is accompanied by a small quantity of the yellow compound **VIII**, [pzH$_2$] [AuCl$_4$], the presence of which is due to the hydrogen chloride resulting from the formation of **VII**.

In conclusion, besides the tetrachloroaurate **VIII**, with Au(III) it is possible to obtain pyrazole adducts (**IV**, **VI**), pyrazolates with (**II**) or without (**III**, **V**) ring chlorination and finally, an uncommon species where both pz$^-$ and pzH are simultaneously present (**VII**).

Experimental

The compound **I** [4], the other pyrazolatogold(I) [3, 5], and anhydrous gold(III) chloride [16] were prepared according to published methods. Evaporation was always carried out under reduced pressure (water aspirator). The analytical determinations were carried out at the Universities of Milan or Saragossa.

{Cl$_2$Au[μ-(3,5-Ph$_2$-4-Cl-pyrazolato-N,N′)]}$_2$, II

The compound **I** was covered with *aqua regia*. After 1.5 h the liquid was removed by decantation, the residue washed with water several times, dried in a desiccator, and crystallized from chloroform/hexane, thus affording the orange compound **II**, yield 50%, m.p. 150–155 °C with dec.. The proton NMR spectrum in CDCl$_3$ showed only a multiplet between 2 and 3τ (aromatic protons); in the infrared spectrum there is a strong vibration at 367 cm^{-1}, assigned to ν(Au–Cl).

{Cl$_2$Au[μ-(Pz-N,N′)]}$_n$, III

This was prepared similarly from AuPz. It is pale yellow, sparingly soluble in acetone or dichloromethane. Infrared spectrum (nujol mull): 3130sh,m, 3120m; 1493m; 1432m; 1318w; 1301s; 1218w; 1299s, 1180m,sh; 1123w; 1056s; 978w; 908w; 880w; 761s; 742s, 726w,sh; 611s. In the low frequency region there is one strong absorption at 375 cm^{-1} with a shoulder at 384 cm^{-1}; in this case it is uncertain which is the Au–Cl stretching frequency because a broad and medium band at 375 cm^{-1} is present in the chlorine-free starting material **Ic**.

AuCl$_3$·(3,5-Me,Ph-pzH), IV

To a filtered CHCl$_3$ solution of gold(III) chloride (307.4 mg, 1.01 mmol), 3-methyl-5-phenylpyrazole (160.3 mg, 1.01 mmol) was added. Addition of hexane gave the compound **IV** (220 mg). In the infrared spectrum there is ν(N–H) at 3300 cm^{-1}, broad, and ν(Au–Cl) at 365 cm^{-1}.

[AuCl$_2$(μ-{3,5-Me,Ph-pz-N,N′})]$_2$, V

Potassium hydroxide in methanol (3.53 ml of a 0.092 N solution) was added to **IV** in methanol. The residue, after evaporation to dryness, was extracted with dichloromethane; the compound **V** precipitated upon addition of hexane to the extract. In the infrared spectrum (nujol mull) there is a weak band at 3120 (ν(C–H) of the azole) and at 3050 (ν(C–H) of the aromatic), but no ν(N–H); in the low-frequency region a band at 372 cm^{-1} is assigned to ν(Au–Cl).

AuCl$_3$·PzH, VI

A dichloromethane solution of gold(III) chloride (303 mg, 1 mmol) and pyrazole (68 mg, 1 mmol) was evaporated to dryness and the residue was crystallized from CH$_2$Cl$_2$/hexane in the presence of diethyl ether (to avoid oil formation), affording the yellow compound **VI**. Infrared spectrum (nujol mull): 3300 broad, m; 3155m; 3135m; 1530w; 1510w; 1482m; 1410m; 1380m; 1358m; 1312w; 1266w; 1178w; 1130s; 1097w; 1073m,sh, 1062s, 1050m,sh; 910w; 883w, 792s; 781s; 768m; 723w; 643s; 600s; *ca.* 490w,broad; 373s,sh, 361s.

$AuCl_2(3,5\text{-}Ph_2Pz\text{-}N)(3,5\text{-}Ph_2pzH)$, VII, and $[3,5\text{-}Ph_2pzH_2][AuCl_4]$, VIII

Anhydrous gold(III) chloride (300 mg, 0.99 mmol) was dissolved in dichloromethane and 3,5-Ph_2pzH (220 mg, 1 mmol) was added. After 30 min. the solution was evaporated to dryness and the oily residue solidified upon stirring under hexane. The solid (265 mg) was extracted with diethyl ether. The extract was concentrated and an orange solid, **VII**, precipitated upon addition of hexane. The residue of the extraction was crystallized from CH_2Cl_2/diethyl ether affording an yellow precipitate, **VIII**. For **VIII** the infrared spectrum (nujol mull) contained: 3500–2200 medium/strong; 1610s; 1582s; 1550w; 1528w; 1430sh; 1412m; 1303w; 1283w; 1259m; 1212sh, 1199w; 1182w; 1090w; 1067w; 1012w; 992w; 960w; 922w; 909w; 816s; *ca.* 760s, broad; 697sh, 672sh, 660s. For **VII** the infrared spectrum contained: 3300m, 3200–2400 medium/strong on which 3130, 3090 and 3060 peaks overlap; 1603w; 1582w; 1563m; 1486s; 1401w; 1353w; 1282w; 1269m; 1209w; 1188w; 1178w; 1072m; 1053w; 1023w; 997w; 972s; 912w; 887w; 812w; 754s; 638s; 552m; 536m, 527sh; 501m; 481m, 474sh; 443w; 371m,sh, 360s.

Acknowledgements

Partial support of this work by 'Consiglio Nazionale delle Ricerche' and by 'Ministero della Pubblica Istruzione' is acknowledged. One of us (M.T.P.) thanks the University of Milan for hospitality during part of this work.

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