*Contribution from the William Ramsay and Ralph Forster Laboratories,
University College, Gower St., London, W.C.1, United Kingdom
and the Istituto di Chimica Generale ed Inorganica,
the University, Padova, Italy*

The Infrared Spectra (450-70 cm^{-1}) of Square Planar Pyridine an Substituted Pyridine Complexes of Gold(III)

L. Cattalini,* R. J. H. Clark, A. Orio,* and C. K. Poon****

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A series of gold(III) complexes of the type $AuX_3 . L$, where L = pyridine, pyridine-d_5, 2-, 3- or 4-methyl pyridine, 2,6-, 3,5- or 2,4-lutidine, or 4-cyanopyridine and X = Cl or Br, have been prepared, the bromo-complexes for the first time, and their infrared spectra have been recorded in the range 450-70 cm^{-1} as nujol mulls. The metal-halogen stretching vibrations in the complexes are assigned, and compared with the corresponding vibrations in the parent AuX_4^- ions. The metal-base stretching vibrations are also assigned where possible, and an attempt is made to correlate these with the strenghts of the bases.

Introduction

In a recent publication,[1] the influence of basicity and steric hindrance on the reactivity of amines towards the tetrachloroaurate(III) ion has been reported. A linear free energy relationship is observed between the second order rate constants and the basicity of the entering groups. Moreover, the steric hindrance associated with the presence of one or two methyl groups in the α-position decreases the reactivity, the effects of the methyl groups being additive.

Table I. Analytical Data on the New Complexes

Complex	Au		C		H		N	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$AuBr_3$. (py)	38.2	37.9	11.6	11.3	0.9_5	0.9_5	2.7	2.7
$AuBr_3$. (2—Me—py)	37.2	37.0	13.6	13.6	1.3_5	1.2_5	2.6_5	2.6
$AuBr_3$. (3—Me—py)	37.2	37.0	13.6	13.5	1.3_5	1.3	2.6_5	2.7
$AuBr_3$. (4—Me—py)	37.2	36.8	13.6	13.6	1.3_5	1.3	2.6_5	2.6_5
$AuBr_3$. (2,6—lut)	36.2	35.8	15.5	15.4	1.6_5	1.6_5	2.6	2.6
$AuBr_3$. (3,5—lut)	36.2	36.1	15.5	15.5	1.6_5	1.6	2.6	2.5_5
$AuBr_3$. (2,4—lut)	36.2	35.0	15.5	15.4	1.6_5	1.7	2.6	2.6
$AuBr_3$. (4—CN—py)	37.4	36.8	13.7	13.5	0.7_5	0.7_5	5.3	5.1
$AuCl_3$. (4—CN—py)	48.3	48.3	17.7	17.6	1.0	1.1	7.1_5	7.0_5

In an attempt to obtain more information about the complexes so formed, namely $AuX_3 . L$, where L = pyridine, pyridine-d_5, 2-, 3- or 4-methyl pyridine, 2,6-, 3,5- or 2,4-lutidine, or 4-cyanopyridine and X = Cl or Br, the infrared spectra of the complexes have now been recorded in the metal-ligand stretching and bending frequency regions (450-70 cm^{-1}). Metal-ligand stretching frequencies are well known[2] to be functions of the oxidation state and coordination number of the metal, but other factors, such as the basicity of the ligand, may also be important.

Experimental Section

The chloro-complexes were prepared as described previously.[3] One of these is new, $AuCl_3$. (4—CN—py), but was prepared by the standard procedure. The bromo-complexes are reported for the first time, and were prepared by adding the amine to an aqueous solution of $HAuCl_4$, neutralised with $NaHCO_3$ and containing 7-8 equivalents of bromide (NaBr or KBr). The gold is initially present in solution almost entirely as the $AuBr_4^-$ ion. The analytical data on the new complexes are given in Table I.

The infrared spectra were recorded as nujol mulls on Grubb-Parsons DM2 and GM3 instruments over the ranges 450-200 and 200-70 cm^{-1} respectively. The spectra were calibrated against that of water vapour. The spectrum of $AuBr_3$(3—Me—py) was also recorded at

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(*) Istituto di Chimica Generale ed Inorganica, Università di Padova, Padova, Italy.

(**) William Ramsay and Ralph Forster Laboratories, University College, Gower St., London, W.C.1, England.

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Table II. Vibrational Frequencies of the AuX_4^- Ions[4,5]

Ion	$\nu_1(a_{1g})$	$\nu_2(b_{1g})$	$\nu_3(a_{2u})$	$\nu_4(b_{2g})$	$\nu_6(e_u)$	$\nu_7(e_u)$	f_{AuX}
	R(ν)	R(ν)	IR(π)	R(δ)	IR,R(ν)	IR,R(δ)	(md/Å)
$AuCl_4^-$	347	324	143	171	356	173	2.10
$AuBr_4^-$	212	196	—	102	252	100	1.76

R = Raman active; IR = Infrared active; ν = stretching mode; π = out-of-plane bending mode; δ = in-plane bending mode; $\nu_5(b_{2u})$ is inactive (note that the assignments for ν_7 and ν_4 are reversed over those given in Refs. 4, 5, owing to the different orientation ot the x- and y-axes).

liquid nitrogen temperatures. The effect of this is to sharpen slightly the whole spectrum, and to raise the frequency of each band by 1 cm^{-1}. The spectra are believed to be accurate to ±1 cm^{-1} for sharp bands and ±2 cm^{-1} for broad bands.

Results and Discussion

The most logical framework on which to base the interpretation of the spectra of the complexes is the spectra of the AuX_4^- ions . These are summarised in Table II, together with their assignments and activities in the D_{4h} point group. The three modes which are eihter completely (a_{1g} and b_{1g}) or essentially (e_u) stretching in character lie in the ranges 324-356 cm^{-1} for X=Cl and 196-252 cm^{-1} for X=Br. The out-of-plane bending mode of the $AuCl_4^-$ ion (a_{2u}) occurs at 143 cm^{-1}, and the in-plane bending modes (b_{2g} and e_u) lie in the ranges 171-173 cm^{-1} for X=Cl and 100-102 cm^{-1} for X=Br.

The vibrational representation of the complexes $AuX_3.L$ in C_{2v} symmetry (the highest possible) is $4a_1+3b_1+2b_2$, all modes being infrared-active. Four of these ($3a_1+b_1$) are essentially stretching modes, three being Au–Cl in character ($2a_1+b_1$) and one Au–L (a_1). The b_1 Au–X stretch correlates with the very intense, e_u mode of the AuX_4^- ion, and is thus likely to be the strongest band in the spectrum of each of the complexes. The a_1 Au–X stretch arising from the symmetric stretching of the *trans* X atoms has a negligible dipole moment change, and is thus likely to lead only to very weak, probably unobserved absorption. The a_1 Au–Cl stretch of the chlorine *trans* to the base is likely to have medium intensity. The out-of-plane (π) an in-plane (δ) bending modes belong ot the representations $2b_2$ and a_1+2b_1 respectively.

The results are given in Table III. In the spectra of most of the complexes there are weak-medium bands in the 400-450 cm^{-1} region which are assigned to ring vibrations of the base.

Gold-Halogen Stretching Vibrations. The most obvious features of the spectra are the very strong bands at 356-366 cm^{-1} for the chlorides and 253-267 cm^{-1} for the bromides. In the light of the discussion above, these bands are assigned unambiguously to the asymmetric (b_1) Au–X stretching vibration of the *trans* halogen atoms. The assignments is further substantiated by near-identity of the frequency ranges to the frequencies of the e_u vibrations of the parent AuX_4^- ions (which have a similar form), and by the narrowness of the frequency ranges (consistent with the atomic motions being at right angles to the Au-base bond in each case). The b_1 Au–X stretching vibration thus behaves as a remarkably good group frequency. Within each range, the 4-cyanopyridine complex gives rise to the highest frequency.

The a_1 Au–X stretching vibration arising from the motion of the halogen atom *trans* to the base proved to be more difficult to identify. This is partly because of its weakness, and partly because it may lie in the region of the metal-base stretching frequency (particularly in the case of the bromides). Despite the tentative nature of the assignments of this mode in Table III, it is clear that its frequency varies quite widely, as expected for a mode which must be strongly coupled with the colinear Au–L stretching vibration.

Table III. Infrared-active Vibrational Frequencies in Complexes of the Type $AuX_3.L$ (450-70 cm^{-1})

Complex	Ligand Modes	ν(AuX)	ν(AuL)[a]			Lower Frequency Bands						
$AuCl_3.(py)$	444 m	362 vs, 333 wm	249 wm, 239 wm				165 ms		129 vs			
$AuBr_3.(py)$	443 wm	260 vs, 225 m	[b]		191 s					111 w		91 s
$AuCl_3.(2\text{—}Me\text{—}py)$	436 m, 402 m	362 vs, 345 sh	249 w			172 m	160 ms		123 s			
$AuBr_3.(2\text{—}Me\text{—}py)$	432 wm, 402 m	262 vs, 236 m	255 ms			186 w	156 s			110 m	105 m	88 m
$AuCl_3.(3\text{—}Me\text{—}py)$	413 m	360 vs, 337 m	234 m, asym			190 m	169 ms		121 s, br			84 m
$AuBr_3.(3\text{—}Me\text{—}py)$	413 m	256 vs, 215 m?	[b]	215 m	194 s	178 s					91 s	87 s
$AuCl_3.(4\text{—}Me\text{—}py)$		356 vs	286 m	212 m	197 w?	183 w	169 ms	145 ms	122 s, br	104 w		
$AuBr_3.(4\text{—}Me\text{—}py)$		254 vs, 202 m?	286 vw?		202 m							81 ms
$AuCl_3.(2,6\text{—}lut)$	408 w, 344 sh	362 vs, 338 sh?	278 w				170 m, br	144 ms	128 s			
$AuBr_3.(2,6\text{—}lut)$	344 wm	253 vs, 224 w?	300 m, 282 m	203 wm					~131 s, br	108 m	99 m	91 m
$AuCl_3.(3,5\text{—}lut)$	427 w	363 vs, 337 w	289 vw?	208 wm		187 m	173 wm, 168 m		127 vs			90 m
$AuBr_3.(3,5\text{—}lut)$	425 w	256 vs, 253 sh	290 wm	208 w?	190 ms	175 ms				104 m		86 s
$AuCl_3.(2,4\text{—}lut)$	444 wm	364 vs, 339 mw	306 w		199 m, br		159 ms	152 m, sh	120 s			
$AuBr_3.(2,4\text{—}lut)$	439 wm	254 vs	299 w	201 w?	190 w			138 m		108 m		85 m
$AuCl_3.(4\text{—}CN\text{—}py)$		366 vs, 339 mw	249 m, 227 wm	202 wm			175 m	148 s	131 s, br	121 s		~94 wm, br
$AuBr_3.(4\text{—}CN\text{—}py)$		267 s	249 vs, 233 wm			182 wm	167 w?	143 s		115 ms		91 m
$AuCl_3.(py\text{—}d_5)$	421 m, 407 m	359 vs	271 m, 263 sh, 227wm		195 wm		166 m	140 s	124 s			84 m
$AuBr_3.(py\text{—}d_5)$	404 wm	258 vs, 213 m	[b]		182 s					109 w		90 s

[a] Suggested assignments. [b] Obscured by ν(AuX). py = pyridine, lut = lutidine, py—d_5 = C_5D_5N, vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

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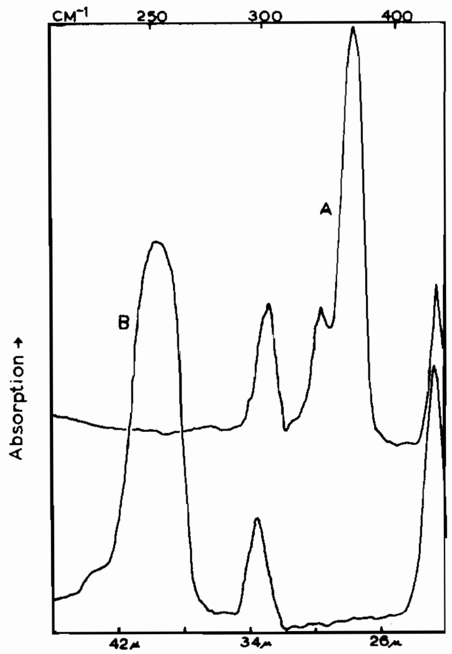

Figure 1. Infrared spectra of (A), $AuCl_3$. (2,4-lut) and (B), $AuBr_3$. (2,4-lut) in the range 455-220 cm^{-1}.

Gold-Base Stretching Frequency. In several cases, considerable difficulty was experienced in attempting to assign the Au–L stretching frequency, again because of coupling of this vibration with the colinear Au–X stretching vibration. A typical spectrum of a chloride and bromide of the same base is shown in Figure 1. The Au–L stretching frequency is assigned tentatively to the range 234-306 cm^{-1}. While the Au–L stretching frequencies appear in general to increase with increase in the base strengths of the ligands (which have pKa's in the order 4–CN–py < py < 3–Me–py < 4–Me–py < 2–Me–py < 3,5–lut < 2,6–lut < 2,4–lut), the irregularities obviously indicate that other factors, such as the mass of the ligands and their degree of steric hindrance, are also important. The relationship is therefore not simple.

Bands below 200 cm^{-1}. The compounds gave good spectra down to 70 cm^{-1} but in the main the bands were not amenable to simple interpretation. All the chlorides had two common features, a medium-strong band at 160-170 cm^{-1} and a strong band at 120-131 cm^{-1}. The former is probably the in-plane and the latter the out-of-plane Cl–Au–Cl bending frequency, by analogy with the corresponding vibrational frequencies of the $AuCl_4^-$ ion (e_u and a_{2u} respectively). The bromides all contain bands of variable intensity in the range 175-202 cm^{-1} (possibly Au–Br stretching modes); they also contain a weak to medium band in the range 104-115 cm^{-1} (exceptions being the 3–Me– and 4–Me–pyridine complexes), and a medium-strong band in the range 81-91 cm^{-1}. These are probably the in-plane and out-of-plane Br–Au–Br bending frequencies.