

SYNTHESIS AND CHARACTERIZATION OF GOLD (III) HALIDE COMPLEXES OF SOME PYRIDINE DERIVATIVES

Mohamed A.S. Goher
Department of Chemistry, Faculty of Science, Alexandria
University, Alexandria, Egypt

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ABSTRACT. Complexes of the types AuX_3L and AuX_3L_2 where L is 2-, and 4-Chloro-, and 4-cyano-pyridines, methyl nicotinate and methyl isonicotinate, and X = Cl or Br, have been prepared and characterized. Their conductivities are measured and discussed. Infrared spectral results suggest that all these ligands function as *monodentates* in the isolated gold complexes. The stereochemistries of the complexes are discussed in relation to the number of stretching gold-halogen frequencies observed in their far infrared spectra.

INTRODUCTION

Complexes of pyridine and its derivatives with first-row transition metal ions have been extensively studied (1). Elman et al. (2,3) and others (4) studied the effects of various substituents on the coordination properties of pyridine-, and quinoline-carboxylic acids and the stereochemistry of the resulting complexes in a search for selective extraction reagents for transition metal ions. On the other hand, gold (III) complexes of variable ligands exemplified by nucleosides (5), triphenyl phosphine (6), pyrimidine (7) heterocyclic dithiocarbamates (8) and other ligands (9) have been recently reported.

In spite of these facts, gold (III) complexes of pyridine and its derivatives have received relatively little attention (10-12). As a part of our studies on the coordination behaviour of pyridine derivative ligands towards gold (III) halides (13,14), we report in this paper the preparation and characterization of those complexes derived from 2-chloro, 4-chloro- and 4-cyano-pyridines, and methyl esters of nicotinic and isonicotinic acids.

EXPERIMENTAL

2-Chloropyridine (2-Clpy), 4-Chloropyridine (4-Clpy), 4-Cyanopyridine (4-Cypy) were obtained from BDH Company. Methyl nicotinate (Me-nic) and methyl isonicotinate (Me-ison) were prepared by the method recommended by Vogel (15) for preparation of ethyl nicotinate.

Preparation of the complexes.

$[Au(2-Clpy)Cl_3]$. Chloroauric acid (0.340 g; 1.0 mmol) dissolved in ethanol (10 cm^3) was mixed with an ethanolic solution (15 cm^3) of 2-chloropyridine (0.107 g; 1.0 mmol). Upon evaporating the solvent to one half its original volume by boiling, cooling the final mixture and standing over several days, yellow crystals of the complex were isolated.

$[Au(4-Cypy)Cl_3]$. This complex was prepared by the method given above except that 4-cyanopyridine (0.106 g; 1.0 mmol) was dissolved in 10 cm^3 boiled water.

$[Au(Me-nic)Cl_3]$. This complex was prepared by mixing methyl nicotinate (0.138

g; 1.0 mmol) dissolved in boiled water (15 cm³) with chloroauric acid (0.338 g; 1.0 mmol) in 10 cm³ ethanol and boiling for about 15 minutes. Upon cooling and standing over several days the complex was separated as yellow microcrystalline powder.

Alternatively, methyl nicotinate (0.132 g; 1.0 mmol) was added to chloroauric acid (0.335 g; 1.0 mmol) in 25 cm³ ethanol, boiling, cooling and standing led to the isolation of the same product.

[Au(Me-ison)Cl₃]. Chloroauric acid (0.670 g; 2.0 mmol) in 10 cm³ ethanol was mixed with 4-Clpy (0.453 g; 4.0 mmol) in 15 cm³ ethanol and boiled for about 5 minutes. The mixture was allowed to stand over several days to separate the complex.

[Au(4-Cypy)₂Cl₂]Cl. 4-Cyanopyridine (0.255 g; 2.5 mmol) and chloroauric acid (0.335 g; 1.0 mmol) were mixed together in 20 cm³ ethanol. The mixture was boiled until its volume reduced to one half, cooled and allowed to stand over several days to separate the complex as orange microcrystalline powder.

[Au(Me-ison)₂Cl₂]Cl. Chloroauric acid (0.662 g; 2.0 mmol) and methyl isonicotinate (0.250 g; 1.8 mmol) were mixed in 20 cm³ ethanol and boiled for about 10 minutes. The mixture was cooled and allowed to stand over several days.

[Au(Me-nic)Br₂Cl]. An aqueous solution (8 cm³) of KBr (0.380 g; 3.1 mmol) was added to chloroauric acid (0.365 g; 1.0 mmol) in 8 cm³ water with stirring. To this mixture Me-nic (0.20 g; 1.5 mmol) dissolved in ethanol (10 cm³) was added and the mixture boiled for 20 minutes and allowed to stand after cooling for several days.

[Au(Me-nic)Be₃]. To an ethanolic mixture of Me-nic (0.272 g; 2.0 mmol) and chloroauric acid (0.358 g; 1.0 mmol) was added an aqueous solution (5 cm³) of KBr (0.651 g; 5.5 mmol). Upon allowing the final mixture to stand over several days the complex was separated as red fine needles.

[AuBr₂Cl(Me-ison)]. This complex was prepared according to the procedure given above for preparation of the corresponding Me-nic complex.

All of the above complexes were isolated in the crystalline form and needed no further recrystallization. They were filtered off at the pump and washed with their mother liquors.

Elemental analysis results of the isolated complexes together with some of their physical properties are given in Table 1.

Physical measurements. The infrared spectral bands of free and coordinated ligands are collected in Table 2. In Table 3 the gold-halogen stretching vibration frequencies are compiled. Conductivity measurements were carried out on 10⁻³ F acetone solutions. The experimental procedures and instruments used for different physical measurements are as described previously (13,14).

RESULTS AND DISCUSSION

The results of the preparative work (table 1) show that complexes of the type AuCl₃L were isolated for all ligands irrespective of the volume and position of the substituent group on pyridine ring. On the other hand, complexes of the type AuCl₃L₂ were isolated only for L = 4-Clpy, 4-Cypy and Me-ison, i.e. for ligands with a substituent group in position 4 in pyridine ring. Substituents in positions 2-, or 3- in pyridine hinder the formation of gold complexes of this type. Thus methyl nicotinate (a 3-substituent pyridine ligand) and 2-Clpy

Table 1. Analytical data

Complex	Color	M	Analysis: Found/Required (%)			
			C	H	N	X
AuCl ₃ (2-Cypy)	yellow orange cryst. Powder	35	14.32	1.10	3.42	34.23
			14.50	0.97	3.36	34.05
AuCl ₃ (4-Cypy)	yellow fine crystals	40	14.67	1.02	3.16	33.86
			14.50	0.97	3.36	34.05
AuCl ₃ (Me-nic)	yellow micro- cryst. Powder	38	17.88	1.21	6.90	26.00
			17.68	0.99	6.87	26.13
AuCl ₃ (Me-ison)	yellow micro- cryst. Powder	43	19.21	1.45	3.24	24.27
			19.07	1.60	3.18	24.17
AuCl ₃ (Me-ison)	yellow crystals	47	19.10	1.52	3.10	24.10
			19.07	1.60	3.18	24.17
AuBr ₂ Cl(Me-nic)	red fine crystals	30	10.00	1.40	2.76	
			15.88	1.33	2.64	
AuBr ₃ (Me-nic)	bright red fine crystals	41	14.78	1.34	2.50	42.56
			14.65	1.23	2.44	41.77
AuBr ₂ Cl(Me-ison)	red fine crystals	39	15.80	1.20	2.46	
			15.88	1.33	2.64	
AuCl ₃ (4-Clpy) ₂	yellow micro- cryst. Powder	132	22.42	1.60	5.43	33.56
			22.63	1.52	5.28	33.45
AuCl ₃ (4-Cypy) ₂	yellow fine	142	28.60	1.34		20.26
			28.16	1.57		20.81
AuCl ₃ (Me-ison) ₂	yellow fine crystals	250	29.60	2.34	4.90	18.50
			29.10	2.44	4.84	18.43

M = molar conductivities in acetone.

Table 2. Infrared spectral data (cm⁻¹).

Compound	ring vibrations	ν C=O	ν C-O
2-Clpy	1585, 1575, 1560, 1545, 1425, 1230, 1020, 602, 410		
Au(2-Clpy)Cl ₃	1615, 1592, 1580, 1565, 1428, 1240, 1038, 625, 440		
4-Clpy	1595, 1565, 1485, 1507, 1215, 665, 660, 405		
Au(4-Clpy) ₂ Cl ₃	1610, 1590, 1500, 1440, 1230, 1030, 670, 415		
Au(4-Clpy) ₂ Cl ₃	1605, 1585, 1500, 1430, 1225, 1020, 670, 415		
4-Cypy	1592, 1580, 1570, 1540, 1420, 1200, 1005, 620, 370		
Au(4-Cypy)Cl ₃	1615, 1605, 1590, 1550, 1430, 1220, 1045, 640, 415		
Au(4-Cypy) ₂ Cl ₃	1620, 1595, 1585, 1560, 1430, 1215, 1050, 645, 410		
Me-nic	1595, 1575, 1555, 1450, 1435, 1170, 1010, 650, 390	1735	1300
Au(Me-nic)Cl ₃	1610, 1588, 1580, 1460, 1440, 1200, 1030, 665, 405	1740	1305
Au(Me-nic)Br ₂ Cl	1605, 1590, 1585, 1455, 1440, 1200, 1025, 655, 410	1730	1300
Au(Me-nic)Br ₃	1610, 1585, 1575, 1450, 1435, 1200, 1025, 660, 410	1735	1305
Me-ison	1590, 1575, 1550, 1440, 1220, 1020, 655, 395	1730	1280
Au(Me-ison)Cl ₃	1610, 1580, 1560, 1450, 1240, 1030, 665, 410	1735	1290
Au(Me-ison)Br ₂ Cl	1610, 1590, 1550, 1450, 1235, 1040, 660, 415	1735	1295
Au(Me-ison) ₂ Cl ₃	1605, 1585, 1560, 1440, 1240, 1040, 665, 415	1735	1290

did not produce complexes of ligand contents higher than 1:1 to AuCl₃ whatever the amount of ligand mixed with chloroauric acid. In this respect methyl nicotinate differs from nicotinic acid itself because nicotinic acid forms H-bonding of the type O--H...O between two carboxylic groups in these 2:1 complexes which stabilise them. Methyl nicotinate, however, is similar to ethyl nicotinate which forms only 1:1 complexes with AuCl₃ and AuBr₃(13).

The molar conductivities of about $35-50 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ found for complexes of the type Aux_3L in acetone are much more less than the values found (16) for uni-univalent electrolyte in this solvent. However, these values are very close to those reported for $[\text{Aux}_3(\text{nicotinic acid})]$ (13) or $[\text{Au}(\text{phen})_2\text{x}]$ (17,18). These low molecular conductivities may be due to the rapid rearrangement:



Complexes of the formula Aux_3L_2 behave as 1:1 electrolytes in acetone (16) and therefore penta-coordinated arrangements around gold atom in these complexes is ruled out. Square planar formulation $[\text{Aux}_2\text{L}_2]^+\text{X}^-$ is therefore assigned for these compounds in solutions.

Infrared spectra

Ligand vibrations. The infrared spectral data given in Table 2 for free and coordinated ligands show that the ring C-C, C-N and other ring vibrations are shifted to higher wave numbers in complexes when compared with those of free ligands. This result is an indication of their coordination via the heterocyclic nitrogens (19-22). For methyl nicotinate and isonicotinate ligands, the appearance of the C=O and C-O stretching vibrations at more or less the same frequencies in the spectra of free and coordinated ligands (Table 2) is an indication that the carbonyl groups of both ligands do not participate in bond formation. The same conclusion is attained for the cyano group of 4-cyanopyridine from the constant position of the ν C-N vibrations of free and coordinated ligand. The infrared spectral results therefore suggest that all ligands under consideration act as *monodentates* in the isolated gold (III) complexes.

Far infrared spectra. Planar complexes of the type MX_3Y are expected to show three infrared-active stretching M-X modes ($2A_2 + B_2$) and one stretching M-Y vibration mode (A_1). Fig. 1 shows that the spectrum of the complex $\text{AuCl}_3(\text{Me-nic})$, exhibits three bands at 370, 358 and 330 cm^{-1} . The first two bands may be assigned to ν_{asym} and ν_{sym} (X-Au-X) and the third to ν Au-X *trans* to L (23).

Table 3. Gold-halogen stretching vibrations (cm^{-1})

Complex	ν Au-Cl	ν Au-Br
$[\text{Au}(2\text{-Clpy})\text{Cl}_3]$	375 m, 358 vs, sp, 330 sh	
$[\text{Au}(4\text{-Clpy})\text{Cl}_3]$	372 vs, 358 m, 325 wm	
$[\text{Au}(4\text{-Cypy})\text{Cl}_3]$	370 sh(m), 363 vs	
$[\text{Au}(\text{Me-nic})\text{Cl}_3]$	370 m, sp, 358 vs, 330 wm	
$[\text{Au}(\text{Me-ison})\text{Cl}_3]$	368 s, 340 s, 320 sh	
$[\text{Au}(\text{Me-nic})\text{Br}_2\text{Cl}]$	345 ms	265 vs, 240 vs
$[\text{Au}(\text{Me-ison})\text{Br}_2\text{Cl}]$	360 s	260 vs, 245 vs
$[\text{Au}(\text{Me-nic})\text{Br}_3]$		260 vs, 240 vs
$[\text{Au}(4\text{-Clpy})_2\text{Cl}_2]\text{Cl}$	368 s, 355 ms	
$[\text{Au}(4\text{-Cypy})_2\text{Cl}_2]\text{Cl}$	370 vs	
$[\text{Au}(\text{Me-ison})_2\text{Cl}_2]\text{Cl}$	370 vs, 355 s, 290 m	

Abbreviations: w = weak, m = medium, s = strong; v = very, sp = sharp

Additionally, the spectrum shows a weak to medium band at 300 cm^{-1} which may be of deformation origin. The corresponding bromide complex of methyl nicotinate exhibits at least two bands associated with ν Au-Br (Fig. 1). The positions of these gold-halide stretching bands are in good agreement with those found for terminal ν Au-X frequencies in gold (III) halide complexes of other ligands (8).



Fig. 1. Far infrared spectra of:
 (A) $[\text{Au}(\text{Me-nic})\text{Cl}_3]$
 (B) $[\text{Au}(\text{Me-nic})\text{Br}_3]$
 (C) $[\text{Au}(\text{Me-nic})\text{Br}_2\text{Cl}]$

In the spectrum of AuBr_2Cl (Me-nic), a medium to strong band appeared at 345 cm^{-1} associated with $n\text{ Au-Cl}$, in addition to two bands at 265 and 240 cm^{-1} due to $\nu\text{ Au-Br}$ (Fig. 1). According to the results given in Table 3, the number of the $\nu\text{ Au-X}$ bands observed in the spectra of AuX_3L and $\text{AuX}_2\text{X}'\text{L}$ complexes are consistent with those expected theoretically and confirm the square planar geometry of these complexes.

However, these results clearly indicate that the position or the volume of the substituent group in pyridine ring, and hence the *monodentate* ligand, has no influence on the frequencies of the Au-X modes in AuX_3L complexes. The appearance of two bands associated with $\nu\text{ Au-Br}$ in the spectrum of the complex AuBr_2Cl (Me-nic) suggest *cis*-arrangement for the two bromine atoms. This is in contrast to that observed for the arrangement of the two bromine atoms in the complex AuBr_2Cl (Me-ison). Its spectrum exhibits a single band at 360 cm^{-1} and 260 cm^{-1} due to $\nu\text{ Au-Cl}$ and $\nu\text{ Au-Br}$ respectively. The appearance of a single $\nu\text{ Au-Br}$ band suggests *trans*-arrangements for the two bromine atoms in this case. The difference is apparently due to the position of the substituent group.

For the complexes of the type AuX_3L_2 in solution which is assumed to have a square planar configuration, i.e. $[\text{AuX}_2\text{L}_2]^+\text{X}^-$, *cis-trans* isomers are expected. For *cis* arrangement two Au-X (A_1+B_1) modes are expected to be IR-active, whereas for *trans* arrangement only one Au-X mode (B_{3u}) is IR-active. On the other hand, if one assumes pentacoordination in the solid state, i.e. AuX_3L_2 , one expects a single Au-X mode (E') to be IR-active for D_{3h} symmetry, and three Au-X modes to be IR-active for C_2 or C_{2v} symmetry. This five-coordination arrangement was borne in mind because the spectrum of the complex $\text{AuCl}_3(\text{Me-ison})_2$ shows three bands at 370 , 355 and 290 cm^{-1} whereas that of $\text{Au}(4\text{-Cypy})_2\text{Cl}_3$ exhibits only one band at 370 cm^{-1} associated with $\nu\text{ Au-Cl}$. Bands around 300 cm^{-1} have been assigned as terminal Au-Cl stretching in some gold (III) complexes of 2-(phenytazo) phenyl (24). Thus the medium band at 290 cm^{-1} is presumed to be due to $\nu\text{ Au-Cl}$ to postulate five coordination for the Me-ison complex.

In fact, stable five-coordinate gold (III) halide complexes have been obtained for some sterically hindered phenanthroline derivative ligands (25,26). However if the 290 cm^{-1} band is of deformation origin, the complex may be formulated as *cis*- $[\text{AuCl}_2(\text{me-ison})_2]^+\text{Cl}^-$ with square planar geometry, similar to that postulated for the species in solution. For $\text{AuCl}_3(4\text{-cypy})_2$ exhibiting a single Au-Cl band, a *trans*-square planar or trigonal bipyramidal five-coordinate structure is possible. The results given in Table 3 suggest that *cis*- $[\text{AuCl}_2(4\text{-Clpy})_2]^+\text{Cl}^-$ may be postulated for the 4-chloropyridine complex. However, penta-coordination could not be ruled out.

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