Displacement by Chloride of Pyridine-2-carboxylate from Dichloro(pyridine-2-carboxylato)gold(III) in Acidic Solution; The Position of Ring Opening

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The kinetics of the reaction $[AuCl_2(N\text{-}O)] + 2Cl^- \xrightarrow{2H^+} [AuCl_4]^- + {}^+HN\text{-}OH$ (where N-O = pyridine-2-carboxylate) have been studied at 25 °C in methanol–water (95:5, v/v). In the presence of excess of chloride, the reaction involves a fast and reversible ring opening with Au–N bond breaking ($K_1 = 3.16$ dm^3 mol^{-1}) and a reversible protonation of the free nitrogen ($K_2 = 640$ dm^3 mol^{-1}, corresponding to a pK_a of 2.80) followed by a typical associatively activated displacement of the *O*-bonded ligand by chloride, with the usual rate law, $k_{obs.} = k_1 + k_2[Cl^-]$ where k_1 (the solvolytic rate constant) = 1.9×10^{-4} s^{-1} and $k_2 = 4.54 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. In the absence of chloride a solvolytic ring opening can be observed but the reaction stops before the monodentate ligand is displaced.

In the substitution reactions of four-co-ordinate planar complexes of the d^8 centres Pd^{II}, Pt^{II}, and Au^{III} the lability of oxygen-donor ligands depends very greatly upon their nature. In particular, the great lability of co-ordinated water (matched by that of other neutral oxygen donors such as CH_3OH) contrasts strongly with the inertness of co-ordinated hydroxide.[1] Any extensive study of this problem is hampered by the lack of suitable substrates because of the synthetic problems involved in preparing appropriate complexes with monodentate ligands.

One way of solving the problem has been to incorporate the oxygen donor in a bi- or multi-dentate ligand. The ring-opening reactions of mixed nitrogen–oxygen chelates of platinum(II) complexes have been examined [2] but nothing has been reported for analogous gold(III) complexes.

The substitution reactions of chelated (bi- or ter-dentate) gold(III) complexes have been restricted to the displacement of nitrogen donors such as 2,2′-bipyridyl,[3] *NNN′N′*-tetraethyl- and -tetramethyl-1,2-diaminoethane,[4] 5-nitro-1,10-phenanthroline,[5] 1,2-diaminoethane,[6] 1,3-diaminopropane,[6] and 3-azapentane-1,5-diamine [7] from their corresponding $[Au(N\text{-}N)Cl_2]^+$ or $[Au(N\text{-}N\text{-}N)Cl]^{2+}$ complexes, generally by Cl$^-$. Short-lived five- and six-co-ordinate intermediates were postulated in order to account for the unusual rate laws sometimes observed. This appears to be a common feature of these reactions, possibly because of the relative inertness of the chelate complexes towards substitution and the electrostatic interactions between the cationic substrate and the anionic nucleophile.

We have synthesized the neutral complex dichloro(pyridine-2-carboxylato)gold(III), $[Au(N\text{-}O)Cl_2]$, and studied the displacement of the chelate by chloride in acidic methanol containing 5% water. The kinetics of the reaction (1) are reported in this paper.

$$[Au(N\text{-}O)Cl_2] + 2Cl^- \xrightarrow{H^+} [AuCl_4]^- + {}^+HN\text{-}OH \quad (1)$$

Experimental

Dichloro(pyridine-2-carboxylato)gold(III).—A solution of pyridine-2-carboxylic acid (0.358 g, 2.91 mmol) in water (30 cm^3) was slowly added, with stirring, to a neutralized solution of $HAuCl_4 \cdot 3H_2O$ (1.15 g, 2.91 mmol) in water (50 cm^3). A pale yellow powder precipitated within a few minutes and was filtered off. The yellow filtrate was placed in a refrigerator and the pale yellow microcrystalline precipitate obtained overnight was filtered off, washed with water, ethanol, and diethyl ether, and dried *in vacuo*, m.p. 166 °C (Found: C, 18.55; H, 1.05; Au, 50.4; Cl, 18.3; N, 3.45. $C_6H_4AuCl_2NO_2$ requires C, 18.45; H, 1.00; Au, 50.5; Cl, 18.2; N, 3.60%). Infrared (Nujol mull between NaCl plates and polyethylene pellets) bands: 1 705vs [ν(C–O), co-ordinated carboxylate group], 1 610m [ν(C=C), co-ordinated pyridine ring], and 380ms cm^{-1} [ν(Au–Cl)]. The microcrystalline product was used in all the kinetic experiments.

Hydrogen tetrachloroaurate(III) trihydrate, pyridine-2-carboxylic acid, hydrochloric acid, perchloric acid, lithium chloride, lithium perchlorate, and the solvent were all reagent grade products.

Kinetics.—The reactions were started by mixing known prethermostatted volumes of a fresh solution of the substrate in methanol–water (95 : 5, v/v) solvent and one containing the appropriate reagents (H$^+$, Li$^+$, Cl$^-$, ClO_4^-) in the same solvent in the thermostatted cell of a Varian–Cary 219 spectrophotometer, at 25 °C. The reactions were followed by scanning the spectrum periodically in the range 250—370 nm and/or measuring the increasing absorbance at 320 nm, as a function of time. In all cases the nucleophile concentration was at least 10 times greater than that of the substrate in order to ensure pseudo-first-order conditions. The values of $k_{obs.}$ were determined from the slopes of plots of ln $(A_\infty - A_t)$ *vs.* time (A_∞ and A_t being the absorbance at the chosen wavelength at the end of the reaction and at time t respectively), by a weighted linear regression analysis. Significant spectra are reported in Figure 1.

Results

It is convenient to present the results in four sections depending upon the experimental conditions.

(1) *Reaction with Chloride at Higher Acid Concentrations* ([H$^+$] ⩾ 0.07 mol dm^{-3}).—When solutions of the complex and a mixture of $HClO_4$, LiCl, and $LiClO_4$ to maintain constant

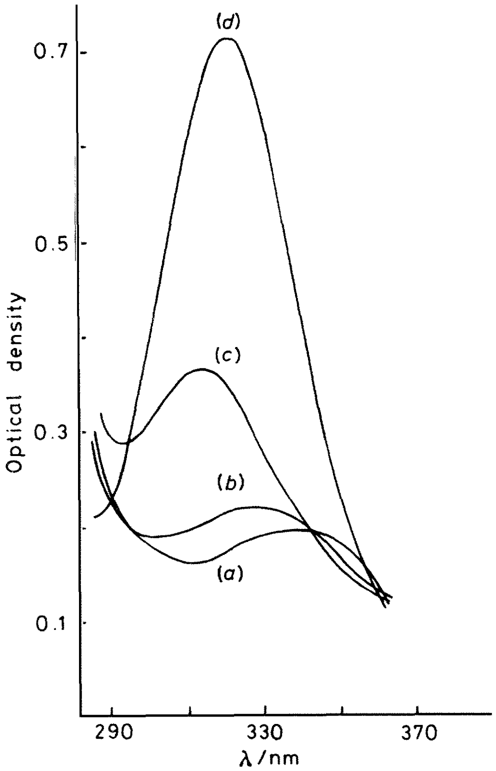


Figure 1. Absorption spectrum of (*a*) $[AuCl_2(N-O)]$ (1.35×10^{-4} mol dm^{-3}), (*b*) solution (*a*) aged with 0.2 mol dm^{-3} $HClO_4$, (*c*) solution (*b*) in the presence of 1.35×10^{-4} mol dm^{-3} LiCl, and (*d*) final solution in the presence of excess of chloride

ionic strength are mixed together there is a rapid change of absorbance in the wavelength range studied (250—370 nm), from spectrum (*a*) to spectrum (*c*) in Figure 1, followed by a slower change in which isosbestic points develop at 294 and 356 nm, from spectrum (*c*) to (*d*) in Figure 1. After this stage has been reached the change of absorbance is first order and the final spectrum corresponds to the sum of the spectra of $AuCl_4^-$ and pyridine-2-carboxylic acid, measured under the same conditions. In some cases the first stage is over before the first measurement is made, but in others the final stages of the first step can be observed. A proper study of the first part requires fast reaction techniques. The first-order rate constants ($k_{obs.}$) obtained from the change in absorbance at a convenient wavelength once the isosbestic points had been established are collected in Table 1, where it will be seen that $k_{obs.}$ is independent of $[H^+]$ and ionic strength but linearly dependent upon $[Cl^-]$, with a relationship of the form $k_{obs.} = k_1 + k_2[Cl^-]$ where $k_2 = (4.44 \pm 0.02) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and $k_1 = (1.9 \pm 0.5) \times 10^{-4}$ s^{-1}. The first-order contribution is small except at the lowest chloride concentrations.

(2) *Reaction with Chloride at Low Acid Concentrations* ($10^{-3} \leqslant [H^+] \leqslant 5 \times 10^{-3}$ mol dm^{-3}).—The spectrophotometric observations are similar to those observed in case (1) with isosbestic points developing after an initial rapid change. The final spectrum between 250 and 370 nm still corresponds to the sum of the spectra of $AuCl_4^-$ and pyridine-2-carboxylic acid measured under the same conditions. The first-order rate constants, $k_{obs.}$, calculated from the second part of the reaction, are collected in Table 2 and are now dependent both on $[H^+]$ and $[Cl^-]$. All reactions were carried out at constant ionic strength (I = 1.0 mol dm^{-3}).

Table 1. First-order rate constants for the reaction of dichloro(pyridine-2-carboxylato)gold(III) with chloride at high acid concentration [a]

$[H^+]$	$[Cl^-]$	I	
	mol dm^{-3}		$10^3k_{obs.}$/s^{-1} [b]
0.5	0.015	1.0	0.96
0.5	0.05	1.0	2.55
0.5	0.075	1.0	3.59
0.5	0.1	1.0	4.58
0.5	0.125	1.0	5.60
0.5	0.15	1.0	6.64
0.5	0.2	1.0	9.14
0.5	0.3	1.0	13.5
0.5	0.5	1.0	22.4
0.57	0.1	1.0	4.60
0.25	0.1	1.0	4.66
0.1	0.1	1.0	4.50
0.07	0.125	1.0	5.64
0.1	0.3	1.0	13.7
0.1	0.05	0.15	2.44
0.5	0.05	0.55	2.51
0.8	0.1	0.9	4.56

[a] Substrate concentration always less than 10^{-4} mol dm^{-3}. [b] Standard errors in rate constants generally less than 5%.

(3) *Reactions with Acid in the Absence of Added Chloride.*—When a solution of the substrate is acidified with methanolic perchloric acid (final $[H^+] \geqslant 0.1$ mol dm^{-3}) its spectrum changes slowly with time [from spectrum (*a*) to (*b*) in Figure 1]. This change is less than that observed in the presence of excess of chloride but a first-order rate law is obeyed until the later stages where subsequent processes can be observed. The final spectrum, before these disturbances, is independent of $[H^+]$ in the range studied. The first-order rate constants ($k_{obs.}$) obtained from the undisturbed part of the reaction are collected in Table 3 where it will be seen that they are independent of $[H^+]$ in the region studied. If small quantities of chloride ($\leqslant 10^{-4}$ mol dm^{-3}) are added the rate of reaction is virtually unchanged but the subsequent interfering reactions appear to be inhibited. The final spectrum in the presence of chloride is considerably different from that measured in its absence, but is similar in many respects to that observed at the beginning of the slow stage of the reaction described in section (1) [spectrum (*c*) in Figure 1]. At lower acid concentrations, $[H^+] < 0.1$ mol dm^{-3}, the final spectrum does depend on the amount of acid present, the amount of change is less, and the associated first-order rate constants increase with decreasing $[H^+]$. The changes were not large enough to make a proper kinetic analysis but the behaviour was consistent with that of an approach to equilibrium with the rate of the reverse reaction increasing as the acid concentration decreased.

(4) *Reactions with Chloride in Aged Acidic Solutions.*—In order to throw more light on the nature of the product formed in case (3) the effect of adding an excess of chloride once the end of the first stage had been reached was studied. Solutions of the complex in perchloric acid ($0.0125 \leqslant [H^+] \leqslant 0.58$ mol dm^{-3}) were allowed to react for a time sufficient for the first stage to be essentially complete but not so long as to allow the ensuing processes to develop. Lithium chloride solution was added and the subsequent spectral changes followed by repetitive scanning in the region 250—370 nm. A very rapid change, that is complete before the first measurement can be made, converted the original spectrum [(*a*) in Figure 1] into one that closely resembled that of the product

Table 2. First-order rate constants for the reaction of dichloro(pyridine-2-carboxylato)gold(III) with chloride at low acid concentration (I = 1.0 mol dm^{-3}) [a]

$[H^+]$ mol dm^{-3}	$[Cl^-]$ mol dm^{-3}	$10^3k_{obs.}$/s^{-1} [b]
0.005	0.75	1.42
	0.1	2.08
	0.15	3.63
	0.2	5.13
	0.25	6.91
	0.3	8.50
	0.4	11.5
	0.5	15.1
0.0025	0.1	1.32
	0.125	1.89
	0.15	2.42
	0.2	3.28
	0.3	6.01
	0.5	11.5
0.002	0.1	1.10
	0.125	1.54
	0.15	2.06
	0.2	3.03
	0.3	5.36
	0.4	7.69
	0.5	9.80
0.001 25	0.1	0.75
	0.125	1.07
	0.15	1.43
	0.2	2.17
	0.3	3.75
	0.5	7.54
0.001	0.1	0.61
	0.125	0.87
	0.15	1.15
	0.2	1.79
	0.25	2.49
	0.3	3.12
	0.35	3.90
	0.4	4.8
	0.5	6.2

[a] Substrate concentration always less than 10^{-4} mol dm^{-3}. [b] Standard errors in rate constants generally less than 5%.

Table 3. First-order rate constants for the reaction of dichloro(pyridine-2-carboxylato)gold(III) in acid solution [a]

$[H^+]$/mol dm^{-3}	$10^4k_{obs.}$/s^{-1} [b]
0.1	2.92
0.1 [c]	2.2
0.2	1.95
0.2	1.91
0.35 [c]	2.2
0.35	2.33
0.5 [c]	2.05
1.0	2.2

[a] Substrate concentration always less than 10^{-4} mol dm^{-3}. [b] Standard error in rate constants generally less than 5%. [c] Chloride ion (10^{-4} mol dm^{-3}) present in solution (see text).

Table 4. First-order rate constants for the reaction of dichloro(pyridine-2-carboxylato)gold(III) with chloride in aged acidic solutions [a]

$[H^+]$ mol dm^{-3}	$[Cl^-]$ mol dm^{-3}	I mol dm^{-3}	$10^3k_{obs.}$/s^{-1} [b]
0.025	0.0125	0.0375	0.83
0.0125	0.025	0.0375	1.23
0.1	0.025	0.125	1.31
0.175	0.025	0.2	1.40
0.1	0.05	0.15	2.27
0.5	0.05	1.0	2.45
0.25	0.05	0.3	2.17
0.58	0.05	0.63	2.50
0.025	0.1	0.125	4.35
0.5	0.1	1.0	4.5
0.25	0.1	1.0	4.6
0.25	0.125	1.0	5.7
0.25	0.15	1.0	7.0

[a] Substrate concentration always less than 10^{-4} mol dm^{-3}. [b] Standard error in rate constants generally less than 5%.

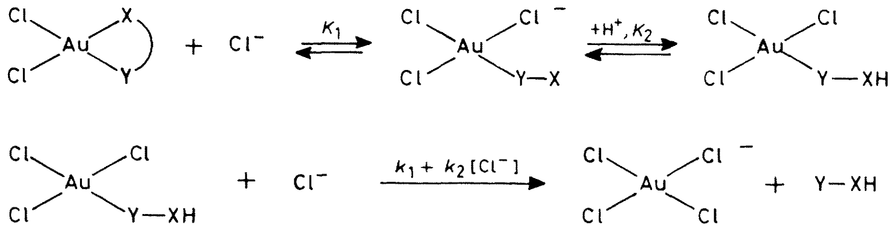
obtained in the presence of small amounts of chloride (10^{-4} mol dm^{-3}), (*c*) in Figure 1. The subsequent changes in absorbance are identical in form to those observed in the first group of experiments and the final spectrum is that of the 1 : 1 mixture of $AuCl_4^-$ + pyridine-2-carboxylic acid. The change in absorbance follows a first-order rate law and the first-order rate constants, $k_{obs.}$ (Table 4), are independent of $[H^+]$ but linearly dependent on $[Cl^-]$. A plot of $k_{obs.}$ *vs.* $[Cl^-]$ has a slope of $(4.43 \pm 0.09) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and intercept $(1.7 \pm 0.7) \times 10^{-4}$ s^{-1}. These values are very similar to those derived from the data in Table 1 and it is concluded that the same reaction has been studied by the two different approaches.

Discussion

The reaction between dichloro(pyridine-2-carboxylato)gold(III) and chloride in acidic 5% aqueous methanol leads to the complete displacement of the chelate ligand and the formation of the $[AuCl_4]^-$ ion. The displacement takes place in two stages, the first being relatively fast and reversible while the second is slow. Under most conditions the two processes are kinetically separable. The simplest representation of this is as in Scheme 1 where the two different ends of the chelate are represented as X and Y.

If the two processes associated with ring opening were sufficiently fast and reversible, then, once the pre-equilibria were established the reaction would be a first-order process with $k_{obs.}$ expressed as in equation (2). When the acid concentration is high enough, it has been observed (Table 1) that $k_{obs.}$ becomes independent of $[H^+]$ and linearly dependent on $[Cl^-]$. The above expression will reduce to such a

$$k_{obs.} = \frac{(k_1 + k_2[Cl^-])K_1K_2[H^+][Cl^-]}{1 + K_1[Cl^-] + K_1K_2[H^+][Cl^-]} \qquad (2)$$



Scheme 1.

form if $K_1K_2[H^+][Cl^-] \gg 1 + K_1[Cl^-]$, which can be achieved at high enough $[H^+]$ if $K_2 \gg K_1$. The expression (2) will then reduce to $k_{obs.} = k_1 + k_2[Cl^-]$ which is the usual form found for associative substitution in planar four-co-ordinate d^8 complexes in solvents that can contribute a solvolytic pathway. Under these circumstances, the substrate will be entirely in the form of the Cl_3Au–Y–XH complex and the conditions in case (1) allow the direct determination of the displacement of this monodentate ligand.

In order to decide whether Au–O fission proceeds or follows Au–N fission it is necessary to compare the rate constants for the final loss of the ligand with those obtained for corresponding monodentate systems. Although no data are available for the displacement of carboxylates from Au^{III}, there has been an extensive study of the displacement of heterocyclic nitrogen bases by chloride.[8] It was found that, in the usual rate law, $k_{obs.} = k_1 + k_2[Cl^-]$, k_1 was insensitive to the basicity of the substituted pyridine, B, while k_2 obeyed the relationship, $\log k_2 = -0.67(pK_a) + C$ (pK_a is that of HB^+ in water at 25 °C). It was also shown[9] that the coefficient (0.67) was insensitive to change in the solvent, although there was a significant variation in k_2. The rate constants for the displacement of pyridine (py) from $[AuCl_3(py)]$ by chloride were determined in the 5% aqueous methanol solvent used in this work; at 25 °C, $k_1 = (1.80 \pm 0.03) \times 10^{-3}$ s^{-1} and $k_2 = (1.62 \pm 0.04) \times 10^{-1}$ dm^3 mol^{-1} s^{-1}. The nitrogen basicity of pyridine-2-carboxylic acid cannot be measured directly because of the zwitterion character of the compound, but it has generally been assumed that since the inductive effects of –COOH and –COOCH$_3$ are likely to be very similar[10] the value of $pK_a = 2.21$ can be used as a measure of this basicity. Using the expression $\log k_2 = -0.67$ $(pK_a) + C$ and the data for pyridine ($pK_a = 5.17$), k_2 for the displacement of *N*-bonded pyridine-2-carboxylic acid is estimated to be 15.6 dm^3 mol^{-1} s^{-1}. This is considerably greater than the observed value of k_2, 4.44×10^{-2} dm^3 mol^{-1} s^{-1}, determined under the limiting conditions. It is therefore concluded that the second stage cannot possibly be assigned to the displacement of a nitrogen-bonded monodentate and it must therefore be assumed that ring opening occurs at nitrogen and the slow stage is displacement of the carboxylate-bonded ligand. Scheme 1 can therefore be refined by identifying X as N and Y as O.

The reaction, when carried out at lower acid concentrations ($1 \times 10^{-3} \leqslant [H^+] \leqslant 5 \times 10^{-3}$ mol dm^{-3}), still has first-order kinetics once the system has settled down, but $k_{obs.}$ is no longer independent of $[H^+]$ and linearly proportional to $[Cl^-]$. In the absence of a suitable curve-fitting computer program, we attempted to check the extent to which the data fitted equation (2) in the following way. As a first approximation we neglected the k_1 term, so that the expression simplified to (3) and a plot of $[Cl^-]/k_{obs.}$ *vs.* $1/[Cl^-]$ for data at a fixed $[H^+]$ should give a straight line with slope $1/k_2K_1K_2[H^+]$ and intercept $(1 + K_2[H^+])/k_2K_2[H^+]$. Indeed, such plots were apparently linear (Figure 2) although slight curvature may be detected in the curve for the lowest $[H^+]$. The intercepts (Table 5), which relate to the data at $[Cl^-] = \infty$, are least sensitive to the omission of the k_1 term, and they do in fact obey the relationship calculated. A plot of intercept against $[H^+]^{-1}$ should be linear, with slope $(K_2k_2)^{-1}$ and intercept k_2^{-1}. The value of k_2 obtained in this way, $(4.45 \pm 0.08) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, is in close agreement with that determined at high acid concentrations. The value of K_2 is 626 dm^3 mol^{-1}.

$$k_{obs.} = \frac{k_2K_1K_2[H^+][Cl^-]^2}{1 + K_1[Cl^-] + K_1K_2[H^+][Cl^-]} \qquad (3)$$

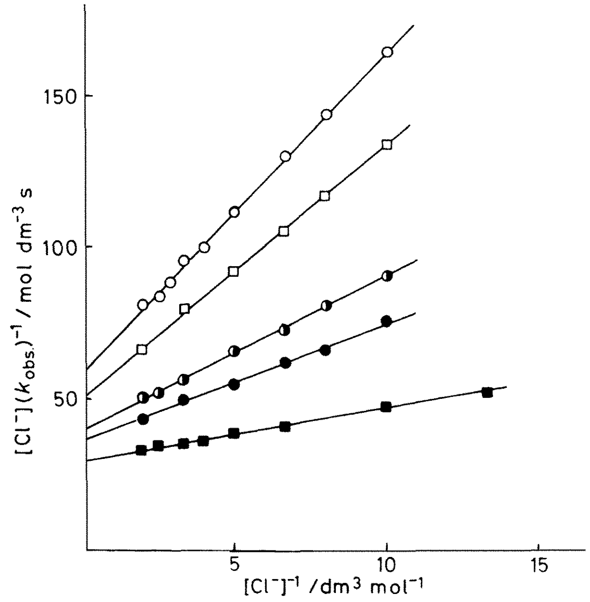


Figure 2. Plot of $[Cl^-]/k_{obs.}$ *vs.* $1/[Cl^-]$ for the reaction $[AuCl_2(N\text{–}O)] + 2\ Cl^- \xrightarrow{H^+} [AuCl_4]^- + {}^+HN\text{–}OH$ at low acid concentrations $[H^+] = 5 \times 10^{-3}$ (■), 2.5×10^{-3} (●), 2×10^{-3} (◑), 1.25×10^{-3} (□), and 10^{-3} mol dm^{-3} (○)

A glance at Table 5 shows that the product of (slope) × $[H^+] = 1/k_2K_1K_2$ is not constant but decreases with increasing acidity. The value of K_1 derived from the simple expression varied from 4.1 to 3.4 dm^3 mol^{-1} as the acid concentration decreased. The full expression was now examined and, using the value of k_1 determined in the stronger acid solutions, K_2, and the average K_1 (3.65 dm^3 mol^{-1}), the correction $k_1K_1K_2[H^+][Cl^-](1 + K_1[Cl^-] + K_1K_2[Cl^-][H^+])^{-1}$ was calculated for each point and subtracted from $k_{obs.}$ to give $k_{corr.}$. Equation (3) now becomes exact if we replace $k_{obs.}$ by $k_{corr.}$. Recycling the data through the above calculation gives a fresh set of linear plots of $[Cl^-]/k_{corr.}$ against $1/[Cl^-]$. The intercepts are hardly changed, except at the lowest $[H^+]$, but the slopes are significantly affected. The re-evaluation gives $k_2 = (4.54 \pm 0.2) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and $K_2 = 640$ dm^3

Table 5. Parameters * from the analysis of the data in Table 4

	Original data				After correction for $k_1 = 1.9 \times 10^{-4}$ s^{-1}			
10^3[H$^+$]	I	S	10^3S[H$^+$]	K_1	I	S	10^3S[H$^+$]	K_1
mol dm^{-3}	mol dm^{-3} s	mol^2 dm^{-6} s	mol^3 dm^{-9} s	dm^3 mol^{-1}	mol dm^{-3} s	mol^2 dm^{-6} s	mol^3 dm^{-9} s	dm^3 mol^{-1}
5	29.8 ± 0.3	1.76 ± 0.05	8.8	4.1 ± 0.3	28.6 ± 0.5	2.22 ± 0.07	11.1	3.1 ± 0.3
2.5	37 ± 2	3.8 ± 0.4	9.6	3.8 ± 0.5	37.3 ± 2.8	4.13 ± 0.45	10.32	3.4 ± 0.5
2	39.8 ± 0.7	5.1 ± 0.1	10.2	3.5 ± 0.2	39.2 ± 0.7	5.55 ± 0.13	11.1	3.1 ± 0.2
1.25	51 ± 1	8.3 ± 0.2	10.4	3.45 ± 0.2	48.7 ± 2.3	8.78 ± 0.35	10.9	3.2 ± 0.2
1	58.9 ± 0.7	10.6 ± 0.1	10.6	3.4 ± 0.2	57.5 ± 0.8	11.49 ± 0.15	11.5	3.0 ± 0.2

Original data:

$I_i = 22.46$ mol dm^{-3} s
$S_s = 3.58 \times 10^{-2}$ mol^2 dm^{-6} s
$k_2 = (4.45 \pm 0.08) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}
$K_2 = 629 \pm 17$ dm^3 mol^{-1}
K_1 (average) $= 3.65$ dm^3 mol^{-1}

After correction:

$I_i = 22.13$ mol dm^{-3} s
$S_s = 3.47 \times 10^{-2}$ mol^2 dm^{-6} s
$k_2 = (4.54 \pm 0.2) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}
$K_2 = 640 \pm 60$ dm^3 mol^{-1}
$K_1 = 3.16 \pm 0.2$ dm^3 mol^{-1}

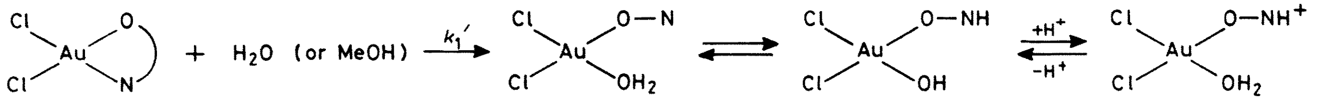
* I and S are the intercepts and slopes of the plots of [Cl$^-$]/$k_{obs.}$ *vs.* 1/[Cl$^-$], I_i and S_s those of the plots of I *vs.* 1/[H$^+$].

mol^{-1} which do not differ significantly from the previous values. The product of (slope) × [H$^+$] becomes reasonably constant, the variation now being random. Using the derived constants, k_1 (1.90 × 10^{-4} s^{-1}), k_2 (4.54 × 10^{-2} dm^3 mol^{-1} s^{-1}), K_1 (3.16 dm^3 mol^{-1}) and K_2 (640 dm^3 mol^{-1}) in equation (2), values of $k_{calc.}$ have been obtained and are collected in Tables 1 and 2.

It is surprising that the treatment is so sensitive to the value of k_1 which is determined with very wide error limits from the reaction under the more concentrated acid conditions, while the derived values of K_1 vary by no more than 10%.

The reactions of the aged acidified solutions with chloride indicate clearly that the process of ageing does not lead to total displacement of the ligand. The immediate change in spectrum on adding excess of chloride leads to one that closely resembles that at the end of the rapid first stage in the first group of experiments, and the close similarity of the form and the rate of the ensuing reaction suggests that the major product at the end of the ageing is oxygen-bonded monodentate dichloro(pyridine-2-carboxylato)(solvent)gold complex (perhaps in equilibrium with some hydroxo-conjugate base). When the ageing is carried out in the presence of small amounts of chloride (10^{-4} mol dm^{-3}) the evidence (spectrum, absence of immediate change of spectrum on adding excess of chloride, identical rate of subsequent reaction) suggests that the product is *O*-bonded trichloro(pyridine-2-carboxylato)aurate.

Since the major product at the end of the ageing process still contains the bidentate ligand bound to gold through oxygen, it is clear that the slow [H$^+$]-independent reaction that leads to the formation of these species cannot be solvolytic displacement of the *O*-bonded ligand in spite of the similarity of the two rate constants (k_1 from the reaction in the presence of excess of chloride = 1.7 × 10^{-4} s^{-1}). The slow ring opening (Scheme 2) would account for the independence of rate on [H$^+$] in the region 0.1 ⩽ [H$^+$] ⩽ 1.0 mol dm^{-3} if the ring opening is irreversible, *i.e.* the stability of the ' zwitterion ' form and/or the full protonation of the ring-opened species forces the equilibrium well over to the right-hand side.



Scheme 2.

The observation that at [H$^+$] < 0.1 mol dm^{-3} the extent of the spectrophotometric change decreases while the rate constant increases for the still first-order change in absorbance confirms the idea that the reaction can be reversible. However, whether this effect comes about from a proton loss from the ' zwitterion ' or the protonated entity cannot be decided on the basis of the information available.

The reaction in the presence of 10^{-4} mol dm^{-3} chloride (a concentration similar to that of the complex) leads to the formation of the $AuCl_3$(O–NH) complex but goes by way of the solvolytic pathway, the concentration of chloride being insufficient for the direct pathway to make a significant contribution to the rate. The observed rate constant for solvolytic ring opening at nitrogen (2.2 × 10^{-4} s^{-1}) is smaller than that for displacement of pyridine from [$AuCl_3$(py)] (1.80 × 10^{-3} s^{-1}) measured under similar conditions. In the displacement of heterocyclic nitrogen bases (am) from [$AuCl_3$(am)] in methanol [8] it has been observed that, whereas k_2 for the reactions with chloride (and bromide) is sensitive to the basicity of am (as discussed above), the solvolytic rate constant is not. Therefore the relatively low value for this rate constant for solvolytic ring opening, probably due to steric restrictions imposed in the act of ring opening,[11] is not contradictory to the rapid pre-equilibrium ring-opening mechanism involved for the reaction in the presence of excess of chloride. We have already established that ' k_2 ' for the ring opening will be large enough to ensure this.

Conclusions

The results presented show quite clearly that the two-stage displacement of pyridine-2-carboxylate from the complex involves a rapid pre-equilibrium ring opening at nitrogen followed by a rate-determining displacement of the monodentate ligand by chloride. There are no studies of monodentate carboxylatogold(III) complexes with which comparison can be made and it is of interest to see that the ' hard ' oxygen donor can be so difficult to dislodge. The analysis of the data at low acid concentration gives a value of 3.2 $dm^3 mol^{-1}$ for the ring-opening equilibrium constant. This can be compared with analogous equilibrium constants for the displacement of monodentate substituted pyridines from $[AuCl_3(am)]$ by chloride, in methanol.[12] There a linear relationship was found between log K and the pK_a of the amine and a long extrapolation to pK_a = 2.2 (the value assigned to the basicity of the nitrogen in pyridine-2-carboxylate) indicates a value of 50. A direct comparison of the two equilibrium constants is meaningless in isolation because they do not have the same dimensions; but a comparison can be made of their ratio (22) with those observed in platinum(II) chemistry for analogous chelate and monodentate systems. For example, a factor of 10^4 has been estimated [13] for the five-membered ring diamine to monoamine ratio in $[Pt(Me_2SO)(en)Cl]^+$ (en = ethylenediamine) which suggests that the chelate effect is less important in the present gold(III) complex than might have been predicted. This problem invites a deeper investigation.

The constant K_2 which has been identified with the protonation of the free nitrogen, 640 $dm^3 mol^{-1}$, is the inverse of the acid dissociation constant of the protonated base; this corresponds to a pK_a of 2.80 which can be compared to a value of 2.21 for the methyl ester. The nitrogen in the co-ordinated difunctional base is thus more basic than that in the methylated (or protonated) analogue. This is the usual pattern of behaviour although the effect seems to be somewhat less than that commonly observed; *e.g.* in $[Pt(Me_2SO)(N{-}N)Cl_2]$, where the pK_a of the co-ordinated amine differs by 1.0 unit from that of the protonated analogue.

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