Displacement of Pyridine-2-methanol from Dichloro(pyridine-2-methanolato)gold(III) in Acidic Solution. Ring Opening at Oxygen

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The kinetics of the displacement of pyridine-2-methanol (N–OH) from dichloro(pyridine-2-methanolato)gold(III), [Au(N–O)Cl$_2$], have been studied in 5% aqueous methanol at 25 °C. In the presence of LiCl and perchloric acid the reaction consists of a pre-equilibrium protonation of the oxygen followed, first, by ring opening at oxygen accompanied by the entry of chloride or solvent, and then by displacement of the *N*-bonded pyridine-2-methanol to give [AuCl$_4$]$^-$. This final stage is very similar to the displacement of 2-(methoxymethyl)pyridine (N–OMe) from [Au(N–OMe)Cl$_3$]. The ligand is not displaced in the absence of chloride. The reaction between [AuCl$_4$]$^-$ and excess pyridine-2-methanol in 5% aqueous methanol was also studied at 25 °C. The initial attachment of the ligand by nitrogen is followed by rapid ring closing and a second molecule of ligand enters more slowly. The final product is [Au(N–O)$_2$]$^+$ (isomeric form unknown), stabilised by the basic conditions generated by the excess ligand. Monodentate pyridine-2-methanol behaves as if it has a pK_a of 5.6 with a steric hindrance comparable to that of 2-methylpyridine.

In a recent paper[1] we discussed the problem of obtaining suitable complexes of gold(III) for the study of the displacement of oxygen donor ligands and suggested that the incorporation of the appropriate donor system in a bi- or multi-dentate ligand provides the required ease of preparation and stability. There we discussed the displacement, by chloride, of pyridine-2-carboxylate from dichloro(pyridine-2-carboxylato)gold(III) and showed that the chelate ring opened at nitrogen and the carboxylate group was displaced in a slower subsequent step. The relative inertness of the Au–OCOR bond has led us to examine the displacement of an alkoxide from Au$^{\mathrm{III}}$, using in this case the chelated pyridine-2-methanolate ligand (N–O). In this paper we report the preparation and characterisation of dichloro(pyridine-2-methanolato)gold(III) and the kinetics of the displacement from it of the bidentate ligand by chloride, equation (1).

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

Experimental

Materials.—Dichloro(pyridine-2-methanolato)gold(III).— Tetrachloroauric(III) acid trihydrate (520 mg, 1.32 mmol) was dissolved in water (50 cm^3) and neutralised with LiOH (144 mg, 1.32 mmol). The solution was treated with pyridine-2-methanol (N–OH) (Aldrich) which had been redistilled under vacuum (55.4 mg, 1.32 mmol). Very soon after mixing an orange-pink precipitate started to separate and, after stirring for 45 min at room temperature, this was filtered off, washed with water, ethanol, and diethyl ether and dried under vacuum. Yield 447 mg (90%), m.p. 136—138 °C.

The reaction can be carried out without adding LiOH. Precipitation is, at first, incomplete (60% yield) but the coloured mother-liquor slowly deposits a much more crystalline sample with the same melting point, elemental analysis, infrared spectrum, and other properties. The crystalline specimen was used for the kinetics. The complex remains unchanged if stored in the dark but will slowly deteriorate when exposed to light (Found: C, 19.1; H, 1.70; Au, 52.2; Cl, 18.7; N, 3.55. $C_6H_6AuCl_2NO$ requires C, 19.2; H, 1.60; Au, 52.4; Cl, 18.9; N, 3.70%). I.r. (Nujol mull between KBr plates or polyethylene pellets) bands at 1 615m, 1 570m (pyridine ring), 355m, 367m [ν(Au–Cl)]. ^{1}H N.m.r. ([$^2H_6$]acetone, SiMe$_4$ internal standard): δ 9.28—7.69 (multiplet, 4 H, pyridine), 5.22 (s, 2 H, –CH$_2$–).

2-(Methoxymethyl)pyridine. Commercial 2-(chloromethyl)-pyridine–hydrogen chloride (Aldrich) (16.2 g) was dissolved in water (100 cm^3) and neutralised to pH 7 by sodium carbonate. Excess sodium chloride was added and the amine extracted with three portions of diethyl ether (25 cm^3 total). The yellow extract was dried and decolourised by adding anhydrous Na_2SO_4 and charcoal and leaving overnight. The colourless filtrate was transferred to a three-necked flask equipped with a dropper funnel, stirrer, nitrogen inlet, and sulphuric acid trap. The apparatus was flushed with dry nitrogen and Na(OMe) [sodium (2.51 g) reacted with methanol (51 cm^3)] was added dropwise over a period of 2 h. The reaction is relatively slow and is accompanied by the precipitation of NaCl. However, Na(OMe) is not very soluble in the diethyl ether–methanol mixture and turbidity early in the reaction is due to its precipitation. The mixture was stirred for a further 24 h under nitrogen, filtered, and the ether and methanol distilled off at atmospheric pressure. The colourless oily residue was distilled under reduced pressure, and the 2-(methoxymethyl)pyridine obtained (b.p. 76—78 °C; 18 mmHg) was identified as its picrate, recovered as yellow crystals from diethyl ether, m.p. 82 °C (lit.,[2] 82—83 °C).

CAUTION. The free base, 2-(chloromethyl)pyridine, is a powerful irritant. Brief exposure, even to the vapour, causes severe pain and a burning sensation to the skin and, if inhaled, a feeling of suffocation and serious irritation to the mucous membrane. The preparation was therefore carried out with extreme care in an efficient fume cupboard and all contact with the skin was avoided.

Trichloro[2-(methoxymethyl)pyridine]gold(III). $HAuCl_4 \cdot 3H_2O$ (500 mg, 1.27 mmol) was dissolved in methanol–water (60:40, 50 cm^3), neutralised with LiOH (30.5 mg, 1.27 mmol) and 2-(methoxymethyl)pyridine (156 mg, 1.27 mmol), dissolved in methanol (2 cm^3), was added. The colour of the solution rapidly changed to yellow and, after *ca.* 15 min, the required product separated as bright yellow crystals which were filtered off, washed with a small amount of cold water, methanol and ether and dried, m.p. 154 °C (Found: C, 19.7; H, 2.10; Cl, 24.8; N, 3.35. $C_7H_9AuCl_3NO$ requires C, 19.7; H, 2.15; Cl, 25.0; N, 3.30%). I.r. (Nujol mull between KBr plates or polyethylene pellets) bands at 1 610m, 1 572m (pyridine ring), 1 090s [ν(O–CH$_3$)], 360m,br [ν(Au–Cl)].

All other chemicals were reagent-grade materials, purified when necessary.

Kinetics.—The reactions were started by mixing known volumes of prethermostatted fresh solutions of (*a*) the substrate in methanol–water (95:5 v/v) and (*b*) the other reagents in the same solvent, in the thermostatted cell of a Varian–Cary 219 spectrophotometer at 25.0 °C. The reactions were followed by scanning the spectrum periodically in the range 240—370 nm and/or by measuring the increasing absorbance at 320 nm, as a function of time. In all cases the concentration of nucleophile was at least 10 times greater than that of substrate in order to ensure pseudo-first-order conditions. The values of the first-order rate constants, $k_{obs.}$, were determined from the slopes of the plots of $\ln(A_\infty - A_t)$ against time (A_∞ and A_t being the absorbances at the chosen wavelength at the end of the reaction and at time t respectively), by either a weighted linear regression analysis program or a non-linear regression analysis of the data. All reactions were carried out at constant ionic strength (I = 1.0 mol dm^{-3}, LiClO$_4$).

Results

Solutions of [Au(N–O)Cl$_2$] in methanol–water (95:5 v/v) are, in the absence of light, relatively inert and obey Beer's law. Slow changes that occur over periods longer than 24 h are rapidly reversed when chloride is added and are identified as solvolysis of co-ordinated chloride. They were not studied in any more detail.

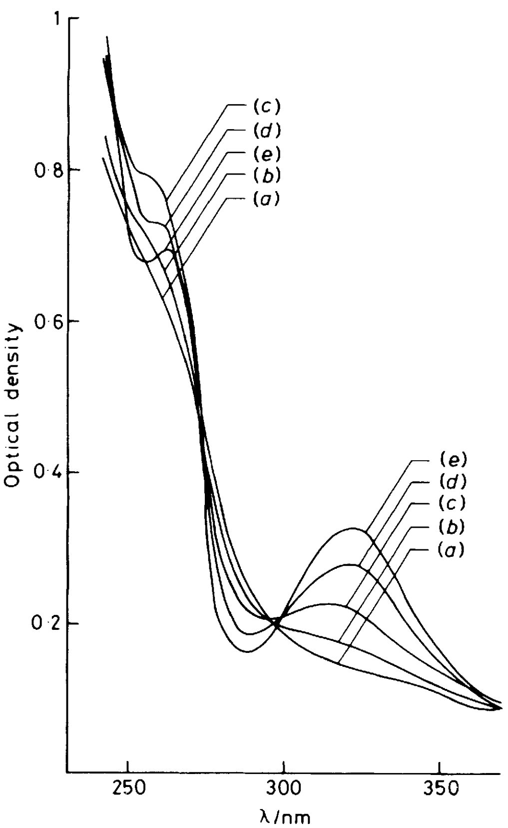


Figure 1. Changes in the spectrum of a solution of [Au(N–O)Cl$_2$] (1.18 × 10^{-4} mol dm^{-3}) and LiCl (1.25 × 10^{-2} mol dm^{-3}) at time t = (*a*) 20, (*b*) 100, (*c*) 200, (*d*) 1 000 s and (*e*) at the end of the reaction

Addition of lithium chloride causes a two-stage change in the spectrum (Figure 1), the first of which is characterised by an increase in absorbance within the ranges 240—270 and 295—360 nm and a decrease within the range 270—295 nm. The reaction is, however, too fast to allow multiple scanning and it is not possible to say whether or not isosbestic points are maintained. The second stage is slow enough to permit multiple scanning and is characterised by isosbestic points at 298 and 362 nm. The final spectrum corresponds exactly to the sum of the spectra of [AuCl$_4$]$^-$ and the free ligand, N–OH, measured under the same experimental conditions. If the solution is also acidified with HClO$_4$ the reaction is very much faster and the change of absorbance with time at a suitable wavelength indicates a two-stage reaction. The final spectrum is that of an equimolar mixture of [AuCl$_4$]$^-$ and the protonated ligand, $^+$HN–OH.

In the absence of lithium chloride, addition of acid leads to a relatively slow change in absorbance that is characteristic of a multi-stage process but addition of LiCl any time after the first stage is complete causes the spectrum to change almost immediately to one that closely resembles that of [Au(N–OMe)Cl$_3$] [N–OMe = 2-(methoxymethyl)pyridine]. The slow stage that follows is identical in every respect to the second stage of the reaction studied in the presence of acid and LiCl.

The kinetics were evaluated from the change in absorbance at a single wavelength (320 nm) where both stages lead to an increase in absorbance. The absorbance–time data were analysed in terms of two successive first-order processes but since the two rate constants differed by factors of at least ten, their separate evaluation presented no problems. Values of the rate constants for the first, $k_{obs.}^{f}$, and second, $k_{obs.}^{s}$, stages are collected in Table 1.

At constant [H$^+$], $k_{obs.}^{f}$ varies with [Cl$^-$] such that a plot of $k_{obs.}^{f}$ *versus* [Cl$^-$] is linear, with a finite intercept (Figure 2), *i.e.*, $k_{obs.}^{f} = a + b[\mathrm{Cl}^-]$. In the absence of added acid the relationship becomes $k_{obs.}^{f} = b_0[\mathrm{Cl}^-]$, any intercept being small when compared to the experimental error. Values of a and b, as a function of [H$^+$], and of b_0 are given in Table 2.

In the absence of added LiCl, $k_{obs.}^{f}$ increases as [H$^+$] increases but reaches a maximum value. A plot of $(k_{obs.}^{f})^{-1}$ against [H$^+$]$^{-1}$ is linear up to [H$^+$]$^{-1}$ ≃ 20 dm^3 mol^{-1} (Figure 3) subsequent departure being consistent with $k_{obs.}^{f}$ remaining larger than expected at the lowest [H$^+$]. However, if the values

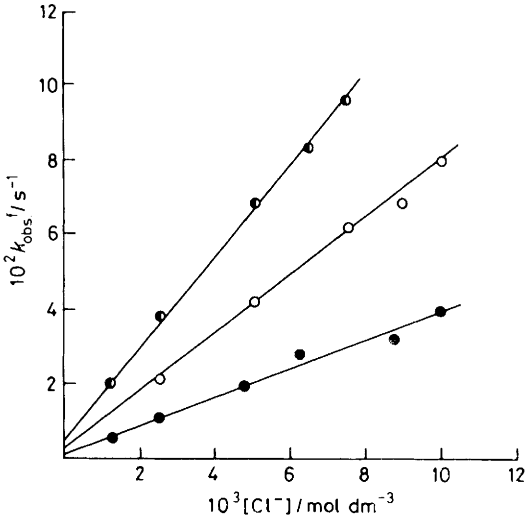


Figure 2. Plots of $k_{obs.}^{f}$ *vs.* [Cl$^-$] for the reaction between [Au(N–O)Cl$_2$] and chloride at [H$^+$] = 0.01 (◐), 0.005 (○), and 0.0025 (●) mol dm^{-3} in MeOH–H$_2$O (95:5 v/v)

Table 1. Observed rate constants ($k_{obs.}$) for reaction (1)[a] at 25 °C in MeOH–H_2O (95:5 v/v)

$[H^+]$/ mol dm^{-3}	$10^2[Cl^-]$/ mol dm^{-3}	$10^2k_{obs.}^{f}$/ s^{-1} [b]	$10^3k_{obs.}^{s}$/ s^{-1} [b]
0.5		4.2	
0.3		4.1	
0.25		4.0	
0.20		3.5	
0.133		3.0	
0.125		2.7	
0.1		2.35	
0.05		1.75	
0.01		0.66	
0.0025		0.535	
0.001		0.455	
	0.25	0.45	0.35
	0.5	0.95	0.38
	1.0	1.45	0.64
	1.25	2.45	0.98
	1.5	2.85	1.35
	2.0		1.45
	2.5		2.05
	3.5		2.60
	4.0		3.15
	5.0		3.80
	6.0		4.65
	7.5		5.85
0.01	0.125	2.05	0.22
0.01	0.25	3.85	0.32
0.01	0.5	6.85	0.505
0.01	0.625	8.3	0.61
0.01	0.75	9.6	0.685
0.005	0.25	2.1	
0.005	0.5	4.15	
0.005	0.75	6.2	
0.005	0.875	6.8	
0.005	1.0	8.0	
0.0025	0.125	0.55	
0.0025	0.25	1.1	
0.0025	0.475	1.9	
0.0025	0.625	2.75	
0.0025	0.875	3.15	
0.0025	1.0	3.95	

[a] I = 1 mol dm^{-3} ($LiClO_4$). [b] Substrate concentration always less than 10^{-4} mol dm^{-3}.

Table 2. Values of the parameters a, b, and b_0 from the data in Table 1 for the groups of experiments at constant added acid

Added acid $[H^+]$/mol dm^{-3}	a/s^{-1}	b/dm^3 mol^{-1} s^{-1}
0.01	(7.1 ± 1.6) × 10^{-3}	12.05 ± 0.3
0.005	(2.2 ± 1.9) × 10^{-3}	7.74 ± 0.26
0.0025	(1.6 ± 1.6) × 10^{-3}	3.71 ± 0.25
		1.94 ± 0.07*

* b_0/dm^3 mol^{-1} s^{-1}.

of the intercepts 'a' from the chloride dependence experiments are included in this treatment, they lie on a continuation of the straight line. Therefore it is probable that the deviations of the directly determined data at low $[H^+]$ are due to interference from a slow parallel solvolytic displacement of co-ordinated chloride. The relationship, $k_{obs.}^{f} = c[H^+]/(1 + d[H^+])$ {characterised by a linear plot of $(k_{obs.}^{f})^{-1}$ against $[H^+]^{-1}$, with a finite intercept} therefore holds when $[Cl^-] = 0$, with c = 0.505 dm^3 mol^{-1} s^{-1} and d = 9.7 dm^3 mol^{-1}. A plot of $b(1 + d[H^+])$ against $[H^+]$ gives a straight line with intercept b_0 and slope e.

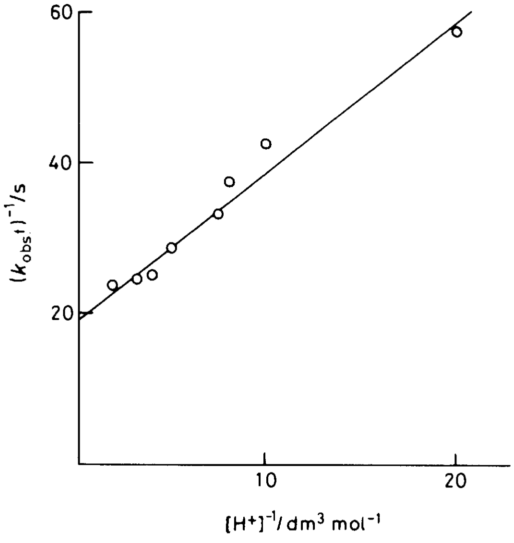


Figure 3. Plot of $(k_{obs.}^{f})^{-1}$ *vs.* $[H^+]^{-1}$ in the absence of chloride

Table 3. Observed rate constants ($k_{obs.}$) and derived rate constants for the reaction $[Au(N\text{-}OMe)Cl_3] + Cl^- \longrightarrow [AuCl_4]^- +$ N-OMe, at 25 °C in MeOH–H_2O (95:5 v/v)[a,b]

$[Cl^-]$/ mol dm^{-3}	$k_{obs.}$/s^{-1}	k_1/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}
0.02	0.002 35	(10 ± 2) × 10^{-4}	(7.93 ± 0.3) × 10^{-2}
0.04	0.004 35		
0.075	0.0071		
0.14	0.012		

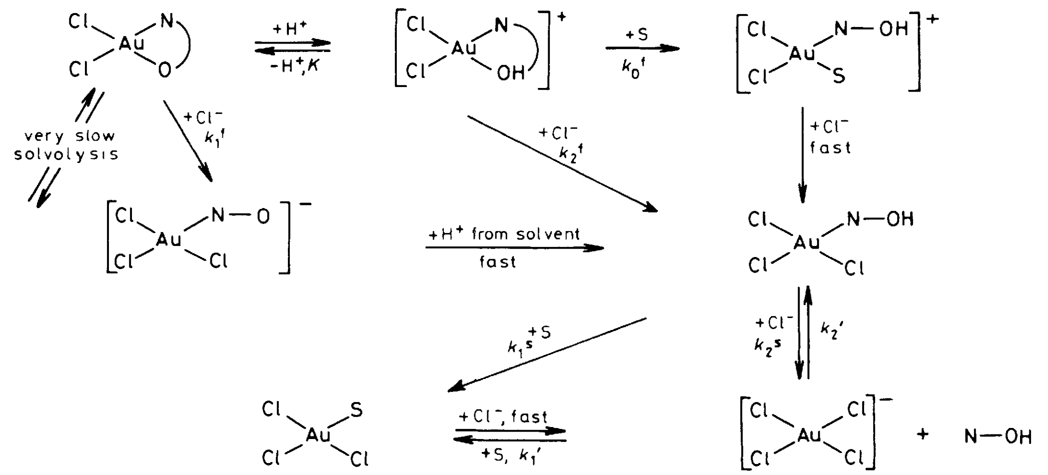
[a] I uncontrolled. [b] Substrate concentration always less than 10^{-4} mol dm^{-3}.

The rate law for the first step therefore takes the form, $k_{obs.}^{f} = (c[H^+] + b_0[Cl^-] + e[H^+][Cl^-])/(1 + d[H^+])$.

The rate constants for the second step of the reaction, $k_{obs.}^{s}$, are independent of $[H^+]$, and obey the simple relationship, $k_{obs.}^{s} = f + g[Cl^-]$, with $f = 7.85 \times 10^{-5}$ s^{-1} and g = 7.58 × 10^{-2} dm^3 mol^{-1} s^{-1}.

The reaction of $[Au(N\text{-}OMe)Cl_3]$ with chloride takes place in a single step, the final spectrum corresponding exactly to that of an equimolar solution of $[AuCl_4]^-$ and the ligand at the same $[Cl^-]$ and $[H^+]$. Plots of $\ln(A_\infty - A_t)$ against time are linear. The first-order rate constants, $k_{obs.}$, were obtained by fitting the A_t *versus* t data to the expression, $A_t = A_\infty - (A_\infty - A_0)\exp(-k_{obs.}t)$ by a non-linear regression with A_0, A_∞, and $k_{obs.}$ as the parameters to be optimised. Values for $k_{obs.}$ thus obtained are collected in Table 3.

The reaction between $[AuCl_4]^-$ and pyridine-2-methanol was studied under conditions where the concentration of the ligand was very much greater than that of the complex. Two consecutive first-order stages can be observed spectrophotometrically and, since the rate constants differ by a factor of *ca.* 10, no problems were encountered in their evaluation. A parallel potentiometric study using a chloride-sensitive electrode showed that each stage corresponded to the release of two chlorides per Au^{III} present. The final product, which was not further characterised, appears to be the bis(pyridine-2-methanolato)gold(III) cation, but the isomeric form is unknown. Both stages of the reaction obey the same rate law, $k_{obs.}' = k_1' + k_2'[N\text{-}OH]$, and $k_{obs.}'' = k_1'' + k_2''[N\text{-}OH]$. Values of $k_{obs.}'$ and $k_{obs.}''$ are collected in Table 4, together with the derived rate constants.



Scheme. $K = 9.7 \pm \text{dm}^3\ \text{mol}^{-1}$, $k_0{}^{\text{f}} = (5.2 \pm 0.7) \times 10^{-2}\ \text{s}^{-1}$, $k_1{}^{\text{f}} = 1.94 \pm 0.03\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, $k_2{}^{\text{f}} = 126 \pm 18\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, $k_1{}^{\text{s}} = (7.85 \pm 3.3) \times 10^{-5}\ \text{s}^{-1}$, $k_2{}^{\text{s}} = (7.58 \pm 0.1) \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, $k_1{}' \simeq 5 \times 10^{-4}\ \text{s}^{-1}$, $k_2{}' = 0.18 \pm 0.01\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$

Table 4. Observed rate constants ($k_{\text{obs.}}$) and derived rate constants for the first and second stage of the reaction between $[\text{AuCl}_4]^-$ and N-OH[a] at 25 °C in MeOH-H_2O (95:5 v/v)[b]

N-OH/ mol dm^{-3}	$k_{\text{obs.}}{}'$/ s^{-1}	$k_{\text{obs.}}{}''$/ s^{-1}	$k_2{}'$/dm^3 mol^{-1} s^{-1}	$k_2{}''$/dm^3 mol^{-1} s^{-1}
0.01	0.002 24	0.000 17		
0.03	0.0059	0.000 45		
0.05	0.009 15	0.000 90	0.18 ± 0.01	(1.66 ± 0.07) × 10^{-2}
0.07	0.014	0.001 15		
0.1	0.018	0.001 65		

[a] *I* uncontrolled. [b] Substrate concentration always less than 10^{-4} mol dm^{-3}.

Discussion

The displacement of pyridine-2-methanol from $[\text{Au(N-O)Cl}_2]$ takes place in two separate successive stages. The first stage corresponds to the opening of the ring by breaking the Au–O bond, the evidence being as follows. (*i*) The second stage of the reaction has a typical rate law associated with the displacement of an *N*-bonded substituted pyridine[3] and the rate constant ($k_2{}^{\text{s}} = 7.58 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$) is comparable to that for the displacement of N-OMe from $[\text{Au(N-OMe)Cl}_3]$ ($k_2 = 7.93 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$). (*ii*) The spectrum of the reaction mixture at the end of the first stage, best obtained by allowing the reaction in the absence of chloride to proceed to completion and then adding LiCl to reverse any solvolysis, is identical to that of a freshly prepared solution of $[\text{Au(N-OMe)Cl}_3]$. (*iii*) It is very unlikely that protonation of the complex would affect the rate constants for the breaking of the Au–N bond to the extent observed. The rate constants are considerably larger than might be estimated from the known relationship between the rate constants and the pK_a of the pyridine being displaced.[3]

The reaction sequence is outlined in the Scheme. If one ignores the solvolytic side-reactions which involve the displacement of co-ordinated chloride and which only interfere at low acid concentrations and in the absence of added chloride, this scheme leads to two consecutive reactions, which, under the conditions [H$^+$], [Cl$^-$], and [complex], are first-order processes of the type, $\text{A} \xrightarrow{k_{\text{obs.}}{}^{\text{f}}} \text{B} \xrightarrow{k_{\text{obs.}}{}^{\text{s}}} \text{C}$, where $k_{\text{obs}}{}^{\text{f}}$ and $k_{\text{obs.}}{}^{\text{s}}$ are defined by equations (2) and (3).

$$k_{\text{obs.}}{}^{\text{f}} = (k_0{}^{\text{f}}K[\text{H}^+] + k_1{}^{\text{f}}[\text{Cl}^-] + k_2{}^{\text{f}}K[\text{H}^+][\text{Cl}^-])/(1 + K[\text{H}^+]) \quad (2)$$

$$k_{\text{obs.}}{}^{\text{s}} = k_1{}^{\text{s}} + k_2{}^{\text{s}}[\text{Cl}^-] \quad (3)$$

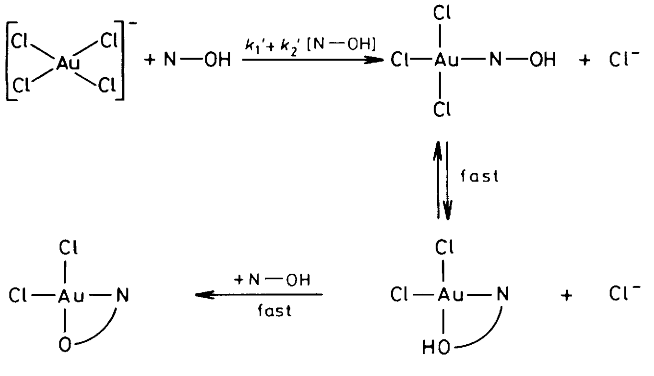
This is in complete agreement with the observed kinetics. The values of the equilibrium constant and the rate constants, which can be related to those extracted from the empirical rate laws: $c = k_0{}^{\text{f}}K$; $d = K$, ($k_0{}^{\text{f}} = c/d$); $b_0 = k_1{}^{\text{f}}$; $e = k_2{}^{\text{f}}K$, ($k_2{}^{\text{f}} = e/d$); $f = k_1{}^{\text{s}}$; $g = k_2{}^{\text{s}}$, are also shown in the Scheme.

The reaction therefore involved a rapid reversible protonation of the alkoxide oxygen, $K = 9.7\ \text{dm}^3\ \text{mol}^{-1}$. The unprotonated ligand can undergo irreversible ring opening at the Au–O bond as a result of direct attack by chloride but there is no evidence for solvolytic ring opening, possibly because the reverse ring closing is very fast. The protonated complex undergoes ring opening both solvolytically and as a direct result of chloride attack. It is interesting to note that, whereas protonation of the alkoxide oxygen does increase its substitutional lability, it only does so by a factor of 65 ($k_2{}^{\text{f}}/k_1{}^{\text{f}}$). In view of the change that protonation causes to the basicity of the leaving group this is quite an important observation and in great contrast to what is found in the reactions of Pt$^{\text{II}}$ and Pd$^{\text{II}}$ complexes. Unfortunately there are, as yet, no quantitative studies to draw on, but general preparative experience and the fact that the solvolytic pathway in aqueous or methanolic solution can be made irreversible by the addition of base through the formation of the substitutionally inert –OH or –OMe species,[4,5] suggests that the relative leaving group effectiveness of H_2O and OH$^-$ (and MeOH and MeO$^-$) is very large indeed in Pd$^{\text{II}}$ and Pt$^{\text{II}}$ chemistry. This is clearly an area that requires a detailed systematic study. Variation in leaving group effectiveness of H_2O/OH^- pairs as the nature of the substrate is changed is well known in Co$^{\text{III}}$ chemistry, although there the substitution is dissociatively activated. Thus, whereas the rate constant for oxygen exchange decreases by at least six orders of magnitude on going from $[\text{Co(NH}_3)_5(\text{H}_2\text{O})]^{3+}$ to $[\text{Co(NH}_3)_5(\text{OH})]^{2+}$,[6] that for the final ring closing in $[\text{Co(edta)L}]^{n-}$ [edta = ethylenediaminetetra-acetate(4−)] changes by less than one order of magnitude on going from L = H_2O (n = 1) to OH$^-$ (n = 2).[7]

The second stage of the reaction, the displacement of the heterocyclic nitrogen base (am) from $[\text{Au(am)Cl}_3]$ by Cl$^-$, can be compared to other reactions of this sort. It has been shown that the second-order rate constant for the direct reaction with chloride, k_2, depends upon the basicity of am according to the relationship, $\log k_2 = -0.67\,(pK_a) + c$ (pK_a is that of amH$^+$ in water at 25 °C).[3] The close similarity of k_2 for the displacement of pyridine-2-methanol and 2-(methoxymethyl)pyridine suggests that they have, effectively, the same basicity. Since k_2 for am = pyridine ($pK_a = 5.17$) is 0.162 dm^3 mol^{-1} s^{-1} (25 °C, 5% aqueous methanol) insertion of the values of k_2 for pyridine-2-methanol (0.0758 dm^3 mol^{-1} s^{-1}) or 2-methoxymethylpyridine (0.0793 dm^3 mol^{-1} s^{-1}) gives them both a pK_a of 5.6. This is larger than the reported value for pyridine-2-methanol, 4.16 (25 °C, H_2O), which, it has been pointed out, is lower than predicted.[8] It has been claimed that the base is stabilised by hydrogen bonding between the alcoholic proton and the nitrogen.[9] This assistance would not be present in the co-ordinated ligand nor in 2-(methoxymethyl)pyridine.

The displacement of pyridine-2-methanol from [Au(N–O)Cl_2] is thus totally different from that of pyridine-2-carboxylate.[1] The carboxylate ligand is displaced in a single reaction stage, ring opening at nitrogen being rapid, reversible and controlled by protonation of the unbound nitrogen. There are two causes for this change of behaviour. Firstly, the change in the 2-substituent from CH_2OH to CO_2^- decreases the basicity of the nitrogen by more than three orders of magnitude and hence increases the lability of the Au–N bond by *ca.* two orders of magnitude. In addition, the bond to the alkoxide oxygen in [Au(N–O)Cl_2] ($k_1^f = 1.94$ dm^3 mol^{-1} s^{-1}) is considerably more labile to direct chloride substitution than the bond to carboxylate in [Au(O–NH)Cl_3] ($k = 4.54 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}) (O–NH = pyridinium-2-carboxylate).[1]

The entry of pyridine-2-methanol into $[AuCl_4]^-$ takes place as shown below. The large excess of ligand provides sufficient base to deprotonate the co-ordinated alcohol group and thereby stabilises the products. The displacement of the second pair of chlorides follows a similar mechanism.



In studies of the reactions between $[AuCl_4]^-$ and pyridines in pure methanol it was shown that the second-order rate constant was related to the basicity of the amine by the expression $\log k_2 = 0.15\,(pK_a) + c$, where c depended upon the amount of steric hindrance generated by substituents in the 2- and 6-positions.[10] The effect of changing the solvent from pure methanol to 5% aqueous methanol has never been studied but, assuming that it does not cause any drastic change, it can be predicted that an entering substituted pyridine of pK_a 5.6 (the value estimated above for pyridine-2-methanol when internal hydrogen bonding is prevented) would give k_2' a value of 1.9 dm^3 mol^{-1} s^{-1} if there is no steric hindrance. If we apply the reduction appropriate to the steric effect of a single methyl group in the 2-position, the predicted value becomes 0.19 dm^3 mol^{-1} s^{-1} which compares closely with the experimental value of 0.18 dm^3 mol^{-1} s^{-1}.

The equilibrium constant for the binding of the heterocyclic nitrogen, K_{am}, in the reaction (4) is given by $K_{am} = k_2'/k_2^s =$

$$[AuCl_4]^- + \text{N–OH} \underset{k_2^s}{\overset{k_2'}{\rightleftharpoons}} [Au(\text{N–OH})Cl_3] + Cl^- \qquad (4)$$

0.18/0.0758 = 2.37. This compares well with the value of k_{am} = 2.39 for am = 2-methylpyridine ($pK_a = 6.10$) in methanol at 25 °C.[10]

Therefore it can be concluded both from the rate constant and the equilibrium constant for complex formation, that the steric hindrance of $-CH_2OH$ in the 2-position is closely comparable to that of $-CH_3$.

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