

Ring Opening and Displacement by Chloride of the Bidentate Chelate Ligand from Dichloro[pyridine-2-(α -methoxymethanolato)]gold(III) – A Kinetic and Mechanistic Study

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The kinetics of ring opening and displacement of the bidentate chelate ligand from dichloro[pyridine-2-(α -methoxymethanolato)]gold(III) [Au(N–O)Cl₂] (**1**) have been studied spectrophotometrically in methanol/water (95:5, v/v) at 25 °C and constant ionic strength ($I = 1 \text{ mol dm}^{-3}$, LiClO₄). In the presence of LiCl and perchloric acid the reaction consists of a pre-equilibrium protonation of the coordinated oxygen followed first by ring opening at oxygen accompanied by the

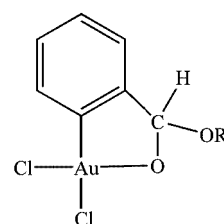
entry of chloride or solvent and fast acetalisation of the hemiacetalic form of the ligand to give [AuCl₃(N–OMe)], and then by displacement of the *N*-bonded ligand to give [AuCl₄][–]. The ligand is not displaced in the absence of chloride and no reaction is observed in the presence of chloride alone.

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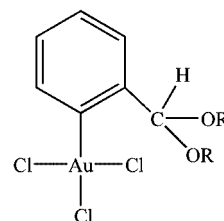
Introduction

The lability of oxygen-donor ligands in the substitution reactions at square planar tetra-coordinate Pt^{II}, Pd^{II} and Au^{III} complexes depends very greatly upon their nature, ranging from the highly labile coordinated water to the very inert hydroxide.^[1] Unfortunately, the lack of suitable substrates of Au^{III}, because of the synthetic difficulties involved in preparing appropriate complexes with monodentate oxygen ligands, has hampered any extensive study in this field. One way to overcome the problem is to incorporate the oxygen donor in a bi- or multidentate ligand so providing the required ease of preparation and stability. Very recently, gold(III) complexes of the type [Au(N–O)Cl₂] (N–O = pyridine-2-methanolato,^[2] substituted pyridine-2-carboxylato^[3]) have been reported to be excellent catalysts in organic synthesis. Some years ago we reported the preparation of dichloro(pyridine-2-carboxylato)gold(III) and dichloro(pyridine-2-methanolato)gold(III) neutral complexes and we studied the replacement of N–O bidentate ligands by chloride in acidic solutions.^[4,5] In the first case it was shown that the chelate ring opened at nitrogen and the carboxylate group was displaced in a slower subsequent step. In the second case, because the change in the 2-substituent from CO₂[–] to CH₂O[–] increases the basicity of the nitrogen by more than three orders of magnitude and hence decreases the lability of the Au–N bond by about two orders of magnitude, and the bond to the alkoxide oxygen is considerably more labile to direct chloride substitution than the bond to carboxylate, the reaction sequence is reversed, ring opening at oxygen occurring in the first stage of the reaction.

In a recent study dealing with the interaction of pyridine-2-carbaldehyde (2CHO–py) with [AuCl₄][–] in water we found^[6] that the initially formed *N*-coordinated [AuCl₃(2-CHO–py)] complex adds a molecule of H₂O to the aldehydic group to form the corresponding diolic derivative which, by elimination of HCl, gives rise to *O*-chelation at the metal centre. Successive treatment with alcohols affords the corresponding N–O-chelated hemiacetalic complexes [**I**], Scheme 1]. On the other hand, when the reaction be-



I: R = –H, –CH₂CH₃, –CH₂CF₃



II: R = –CH₃, –CH₂CH₃, –CH₂CH₂CH₃, –CH₂CH₂CH₂CH₃

Scheme 1.

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tween pyridine-2-carbaldehyde and $[\text{AuCl}_4]^-$ is carried out in alcohols at 60 °C, the *N*-coordinated acetal complexes trichloro(pyridine-2-carbaldehyde dialkyl acetal)gold(III) are directly formed [(II), Scheme 1]. Some of the complexes of both the series have been characterised by X-ray diffractometry.^[6]

As an extension of that work, we have now prepared the analogous neutral dichloro[pyridine-2-(α -methoxymethanolato)]gold(III) (**1**), $[\text{Au}(\text{N}-\text{O})\text{Cl}_2]$, and have studied the displacement of the new type of N–O chelate ligand by chloride in acidic methanol containing 5% water.

Results

The electronic spectrum in the wavelength range 250–370 nm of a 1×10^{-4} mol dm⁻³ solution of $[\text{Au}(\text{N}-\text{O})\text{Cl}_2]$ (**1**) in methanol/water (95:5 v/v) in the presence of a large excess of LiCl to suppress any solvolysis is shown in Figure 1 (curve *a*). This spectrum does not change over long periods of time.

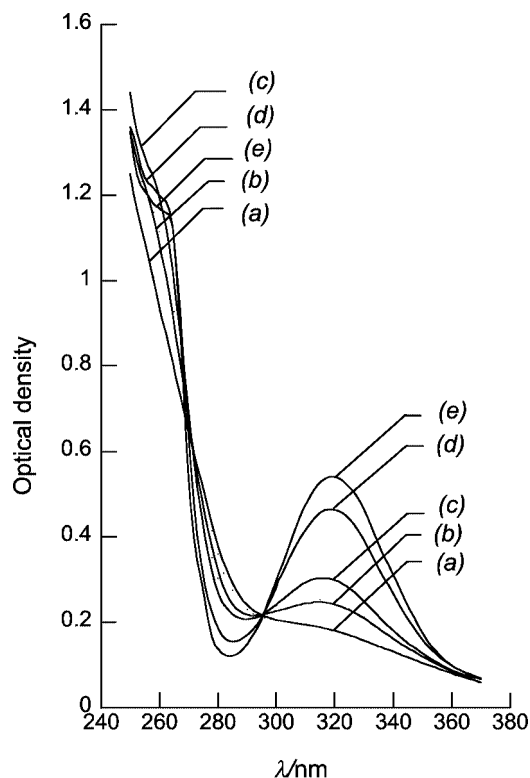


Figure 1. Electronic spectra of 1.0×10^{-4} mol dm⁻³ solutions of **1** in methanol/water (95:5 v/v) at 25 °C under the different experimental conditions reported in the text.

In the absence of lithium chloride, addition of perchloric acid to a solution of **1** of the same concentration causes a relatively fast change of the spectrum with time to finally give the spectrum represented by curve *b*. Successive addition of 1:1 LiCl gives rise to a rapid change of the spectrum *b* to that of curve *c*, which is identical to that of the trichloro(pyridine-2-carbaldehyde dimethyl acetal)gold(III) (**2**) measured under the same experimental conditions. Fur-

ther addition of excess LiCl results in a slower reaction, which leads to the displacement of the 2-substituted pyridine ligand and formation of $[\text{AuCl}_4]^-$ with a well-maintained isosbestic point at 296 nm until the end of the reaction (curves *d*, *e*). When an excess of both LiCl and perchloric acid is added to a solution of **1**, the change of absorbance with time at 320 nm indicates a two-stage reaction, the second stage being identical to that described above.

Table 1. Observed rate constants: for the first stage (k_{obs}^f), for the second stage (k_{obs}^s) of the reaction,^[a] and in the presence of perchloric acid alone (k'_{obs}^f).

$[\text{H}^+]$ [mol dm ⁻³]	$10^3 [\text{Cl}^-]$ [mol dm ⁻³]	$10^2 k_{\text{obs}}^f$ [s ⁻¹]	$10^4 k_{\text{obs}}^s$ [s ⁻¹]	$10^3 k'_{\text{obs}}^f$ [s ⁻¹]
0.15				3.69
0.2				4.47
0.25				5.64
0.3				6.40
0.4				7.60
0.5				9.33
0.05	1.0	0.29		
0.05	2.0	0.72		
0.05	4.0	1.22		
0.05	6.0	1.82		
0.05	8.0	2.40		
0.05	10	3.0		
0.05	12	3.70		
0.1	1.0	0.96		
0.1	2.0	1.67		
0.1	4.0	2.85		
0.1	6.0	4.05		
0.1	8.0	5.11		
0.1	10	6.40		
0.1	12	7.58		
0.15	1.0	1.56	0.99	
0.15	2.0	2.30	1.85	
0.15	3.0	3.20	2.56	
0.15	4.0	4.05	2.91	
0.15	5.0	4.61	3.90	
0.15	6.0	5.30		
0.15	7.0	6.14	5.40	
0.15	8.0	6.89	6.20	
0.15	9.0	7.60		
0.15	10	8.40	7.93	
0.2	1.0	2.50		
0.2	2.0	3.51		
0.2	3.0	4.82		
0.2	4.0	5.82		
0.2	5.0	6.61		
0.2	6.0	7.82		
0.2	7.0	8.90		
0.2	8.0	9.85		
0.2	9.0	11.4		
0.2	10	12.55		
0.3	1.0	3.22		
0.3	2.0	4.84		
0.3	3.0	6.0		
0.3	4.0	7.48		
0.3	5.0	9.01		
0.4	1.0	3.57		
0.4	2.0	5.30		
0.4	3.0	7.60		
0.4	4.0	9.10		
0.4	5.0	10.38		

[a] $I = 1$ mol dm⁻³, LiClO_4 , [substrate] = 1×10^{-4} mol dm⁻³, 25 °C, MeOH/H₂O (95:5 v/v); rate constants were accurate to within 5%.

Kinetics

The kinetics were evaluated from the change in absorbance at a fixed wavelength (320 nm) where both stages lead to an increase of absorbance and as the two rate constants differed by at least ten, their separate evaluation presented no problem. Values of the rate constants for the first, k_{obs}^f , and second, k_{obs}^s , stages of the reaction in the presence of both LiCl and perchloric acid under pseudo-first-order conditions, as well as in the presence of perchloric acid alone, are collected in Table 1. Rate constants were accurate to within 5%.

At constant $[\text{H}^+]$, k_{obs}^f varies with $[\text{Cl}^-]$ such that a plot of k_{obs}^f versus $[\text{Cl}^-]$ is linear with a finite intercept (Figure 2), according to Equation (1).

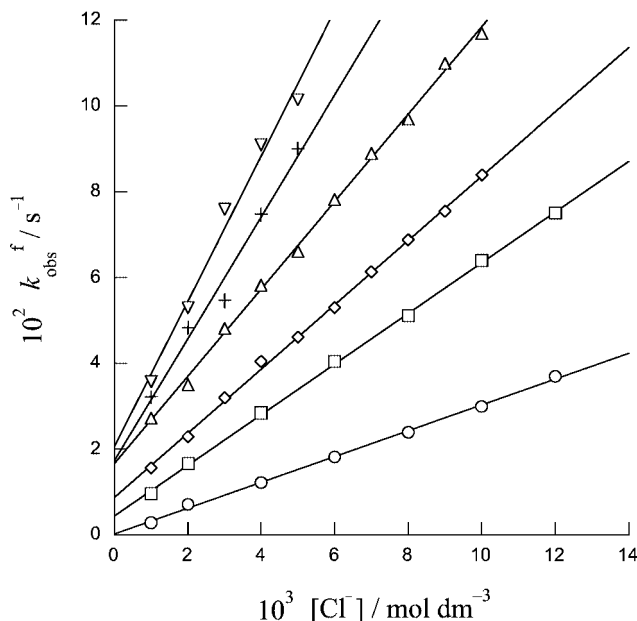


Figure 2. Plots of k_{obs}^f vs $[\text{Cl}^-]$ for the reaction between $[\text{Au}(\text{N}-\text{O})\text{Cl}_2]$ (I) and chloride at $[\text{H}^+] = 0.05$ (O), 0.1 ($\square$), 0.15 ($\diamond$), 0.2 ($\triangle$), 0.3 (+), 0.4 (∇) mol dm^{-3} .

$$k_{\text{obs}}^f = i + s[\text{Cl}^-] \quad (1)$$

Both i and s depend upon $[\text{H}^+]$ as shown in Figure 2 and Table 2.

Table 2. Values of parameters i and s at constant added acid.

$[\text{H}^+]$ [mol dm^{-3}]	i [s^{-1}]	s [$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$]
0.4	$(1.9 \pm 0.3) \times 10^{-2}$	17.4 ± 0.1
0.3	$(1.8 \pm 0.1) \times 10^{-2}$	14.2 ± 0.4
0.2	$(1.3 \pm 0.1) \times 10^{-2}$	10.9 ± 0.2
0.15	$(0.87 \pm 0.05) \times 10^{-2}$	7.52 ± 0.08
0.1	$(0.43 \pm 0.04) \times 10^{-2}$	5.95 ± 0.06
0.05	$(0.03 \pm 0.04) \times 10^{-2}$	3.01 ± 0.05

The dependence of s upon $[\text{H}^+]$ shows a tendency to slow negative deviations as $[\text{H}^+]$ progressively increases, but a plot of s^{-1} against $[\text{H}^+]^{-1}$ is linear (Figure 3) with intercept $c = (1.8 \pm 0.5) \times 10^{-2} \text{ s}^{-1}$ and slope $d = (1.6 \pm 0.5) \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$, from which the empirical Equation (2) can be derived.

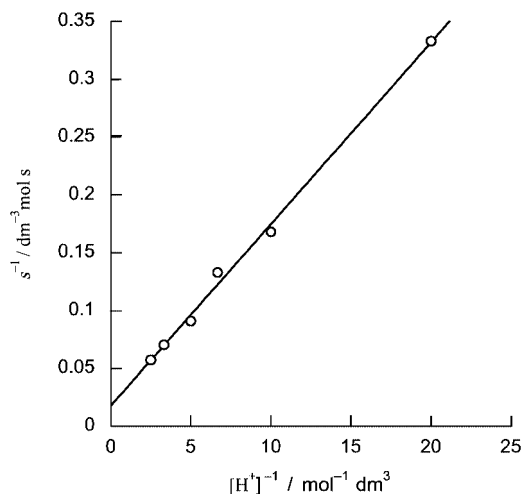


Figure 3. Linear dependence of s^{-1} on $[\text{H}^+]^{-1}$. Data from Table 2.

$$s = \frac{[\text{H}^+]}{c[\text{H}^+] + d} \quad (2)$$

Owing to the large uncertainty in the values of i , its dependence on $[\text{H}^+]$ was better determined on studying the reaction in the absence of added LiCl. The values of the relative rate constants ($k'_{\text{obs}}^f \equiv i$) are collected in Table 1. k'_{obs}^f increases as $[\text{H}^+]$ increases but appears to reach a limiting value at the higher $[\text{H}^+]$ concentrations. A plot of $(k'_{\text{obs}}^f)^{-1}$ against $[\text{H}^+]^{-1}$ is linear in the range of examined $[\text{H}^+]$ (Figure 4) with intercept $e = (40 \pm 6) \text{ s}$ and gradient $f = (35 \pm 1) \text{ mol dm}^{-3} \text{ s}^{-1}$.

These results are in agreement with Equation (3).

$$k'_{\text{obs}}^f = \frac{[\text{H}^+]}{e[\text{H}^+] + f} \quad (3)$$

On substituting Equations (3) and (2) into Equation (1), the experimental rate law for the first step of the reaction

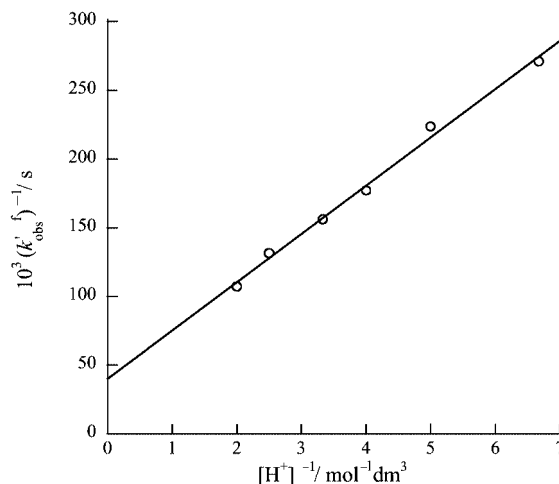


Figure 4. Plot of $(k'_{\text{obs}}^f)^{-1}$ against $[\text{H}^+]^{-1}$ in the absence of added chloride.

takes the form of Equation (4) which can be rearranged as Equation (5) with e/f ($1.14 \pm 0.05 \text{ mol}^{-1} \text{ dm}^3$) = c/d ($1.1 \pm 0.4 \text{ mol}^{-1} \text{ dm}^3$) within the limit of the experimental error and an average value of 1.12 ± 0.03 .

$$k_{\text{obs}}^f = \frac{[\text{H}^+]}{e[\text{H}^+] + f} + \frac{[\text{H}^+][\text{Cl}^-]}{c[\text{H}^+] + d} \quad (4)$$

$$k_{\text{obs}}^f = \frac{\frac{1}{f}[\text{H}^+]}{1 + \frac{e}{f}[\text{H}^+]} + \frac{\frac{1}{d}[\text{H}^+][\text{Cl}^-]}{1 + \frac{c}{d}[\text{H}^+]} \quad (5)$$

The rate constants for the displacement of the *N*-coordinated pyridine ligand, k_{obs}^s (Table 1), are independent from $[\text{H}^+]$ and obey the usual relationship Equation (6) with $g = (2 \pm 1) \times 10^{-4} \text{ s}^{-1}$ and $h = (7.6 \pm 0.2) \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ (Figure 5).

$$k_{\text{obs}}^s = g + h[\text{Cl}^-] \quad (6)$$

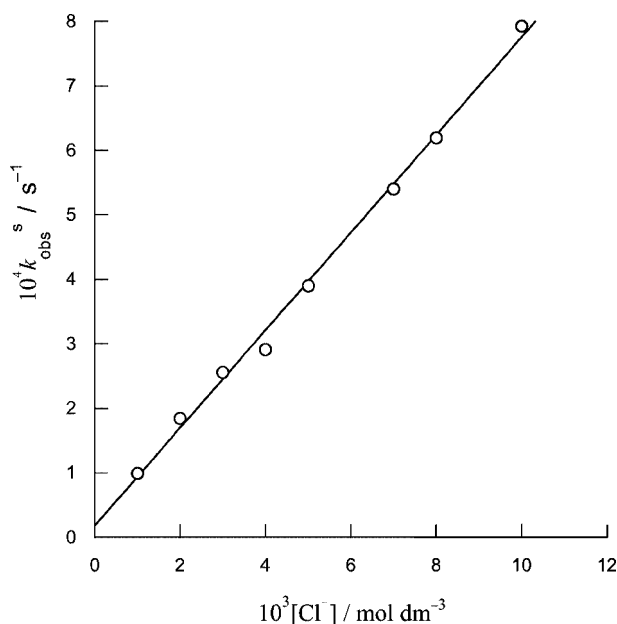


Figure 5. Plot of k_{obs}^s against $[\text{Cl}^-]$. Data from Table 1.

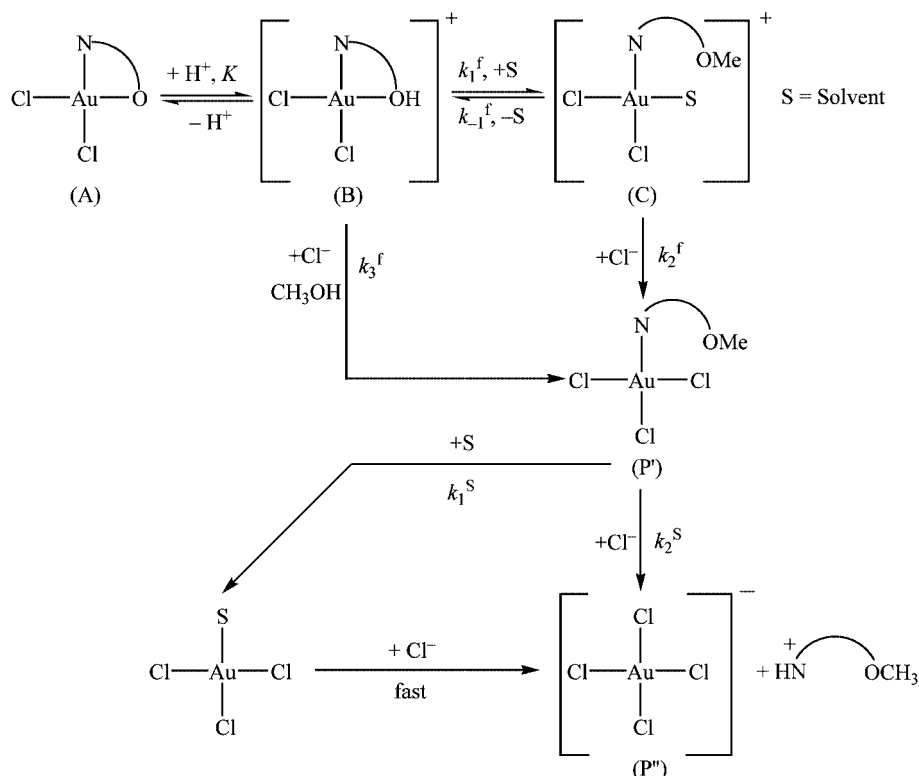
Discussion

The spectroscopic evidence together with the kinetic results are fully consistent with the reaction depicted in Scheme 2.

The reaction observed in the presence of HClO_4 alone is described as a fast protonation pre-equilibrium $\text{A} \rightleftharpoons \text{B}$ followed by a slow reversible reaction to give the solvato species **C** (spectrum *b* in Figure 1). **C** is formulated as the acetalic species, assuming that acetylation of the hemiacetalic group is a fast process in acidic media (see below). Addition of an equimolar amount of LiCl rapidly affords the anation product **P'** (spectrum *c* in Figure 1). The same species can also be formed directly from **B** by reaction with Cl^- . In the presence of higher $[\text{Cl}^-]$, such as those used under pseudo-first-order conditions, displacement of the *N*-coordinated ligand through two parallel reactions, solvolysis and direct chloride substitution, occurs to give the final product **P''**. This latter process corresponds to the second stage of the reaction observed in the kinetic runs, better followed in the presence of chloride ions in acidic solution. The derived rate law, $k_{\text{obs}}^s = k_1^s + k_2^s[\text{Cl}^-]$ typical for the displacement of *N*-bonded pyridines is obeyed,^[7] with a solvolytic rate constant $k_1^s = (2 \pm 1) \times 10^{-4} \text{ s}^{-1}$ and the second-order rate constant $k_2^s = (7.6 \pm 0.2) \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ nearly equal, within the limit of experimental error, to that relative to the displacement of the *N*-coordinated dimethyl acetal ligand from the trichloro(pyridine-2-carbaldehyde dimethyl acetal) gold(III) complex (**2**), [$k_2 = (7.875 \pm 0.003) \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$], kinetically measured under the same experimental conditions, as well as to those found for the displacement of the strictly related pyridine-2-methanol ($k_2 = 7.58 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) and 2-methoxymethylpyridine ($k_2 = 7.93 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$).^[5] Values of k_{obs} for the displacement of the ligand from the trichloro(pyridine-2-carbaldehyde dimethyl acetal)gold(III) complex (**2**) and the derived rate constants are reported in Table 3.

The close resemblance of the electronic spectra of the intermediate formed at the end of the first stage of the reaction and that of complex **2**, as well as the values of their second-order rate constants quoted above for the final displacement of the ligand, strongly support the conclusion that the hemiacetalic form of the chelated ligand, once protonated and then O-opened, undergoes a rapid process of acetalisation in the presence of the solvent MeOH under acidic conditions to give the derived *N*-coordinated dimethyl acetal as the true leaving 2-substituted pyridine in the second stage of the reaction. This behaviour is in agreement with the instability of the hemiacetals of the free organic carbaldehydes^[8] that, under comparable experimental conditions, react with alcohols to rapidly give the corresponding acetals. This conclusion has been fully confirmed by the series of ^1H NMR experiments reported in Figure 6.

When dichloro[pyridine-2-(α -methoxymethanolato)]gold(III) (**1**) in CD_3NO_2 [integrated proton ratio C–H ($\delta = 5.45 \text{ ppm}$)/O–CH₃ ($\delta = 3.56 \text{ ppm}$) of 1:3] (spectrum **A**) is added to methanol and DCl [molar ratio 5:1 and 1:1 with respect to the concentration of complex **1** ($2.56 \times 10^{-2} \text{ mol dm}^{-3}$)] its spectrum rapidly changes (spectrum **B**) to that of an authentic sample of the trichloro(pyridine-2-carbaldehyde dimethyl acetal)gold(III) (**2**) in CD_3NO_2 at a similar concentration ($2.34 \times 10^{-2} \text{ mol dm}^{-3}$) (spectrum **C**), both of them showing an integrated proton



Scheme 2. $K = 1.12 \pm 0.03 \text{ dm}^3 \text{ mol}^{-1}$, $k_3^f = 56 \pm 17 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_1^f = 0.025 \pm 0.001 \text{ s}^{-1}$, $k_1^s = (2 \pm 1) \times 10^{-4} \text{ s}^{-1}$, $k_2^s = (7.6 \pm 0.2) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Table 3. Observed rate constants (k_{obs}) and derived rate constants (k_1 and k_2) for the reaction $[\text{Au}(\text{N-OMe})\text{Cl}_3] + \text{Cl}^- \rightarrow [\text{AuCl}_4]^- + \text{HN-OMe}$ at 25 °C in MeOH/H₂O (95:5 v/v).

$[\text{Cl}^-]$ [mol dm ⁻³]	$10^3 k_{\text{obs}}$ [s ⁻¹]	k_1 [s ⁻¹]	k_2 [mol ⁻¹ dm ⁻³ s ⁻¹]
0.01	0.84	$(5 \pm 3) \times 10^{-5}$	$(7.875 \pm 0.003) \times 10^{-2}$
0.02	1.68		
0.03	2.44		
0.04	3.13		
0.08	6.34		
0.1	7.96		

ratio C–H ($\delta = 6.15 \text{ ppm}$)/O–CH₃ ($\delta = 3.66 \text{ ppm}$) of 1:6. Further addition of DCl [molar ratio 10:1 with respect to the concentration of complex **1**] allows the reaction to go to completion with release of the ligand in the form of the *N*-protonated pyridine-2-carbaldehyde dimethyl acetal [integrated proton ratio C–H ($\delta = 6.02 \text{ ppm}$)/O–CH₃ ($\delta = 3.64 \text{ ppm}$) of 1:6], as comes from a comparison of its spectrum (spectrum **D**) with the spectrum of the released ligand from **2** under the same experimental conditions (spectrum **E**). Spectrum **B** shows also the presence of some free *N*-protonated pyridine-2-carbaldehyde dimethyl acetal as a result of the incoming development of the second stage of the reaction.

From the reaction in Scheme 2, on assuming species C as a steady-state intermediate $\{dC/dt = 0\}$ which implies that

$(k_{-1}^f + k_2^f[\text{Cl}^-]) \gg k_1^f$, the following dependence of k_{obs}^f on $[\text{H}^+]$ and $[\text{Cl}^-]$ is derived [Equation (7)].

Because under our experimental conditions in the presence of $[\text{H}^+] \geq 0.05 \text{ mol dm}^{-3}$ alone, the reaction is completely shifted towards the solvato species C, the condition $k_{-1}^f \ll k_1^f$ must hold and hence, in the presence of Cl^- , the condition $k_2^f[\text{Cl}^-] \gg k_{-1}^f$ must be satisfied. Under these conditions Equation (7) reduces to Equation (8).

Equation (8) is identical to the empirical Equation (5) if $k_1^f K = 1/f$, $K = e/f$, $k_3^f K = 1/d$, from which the values of the equilibrium constant ($K = 1.12 \pm 0.03 \text{ dm}^3 \text{ mol}^{-1}$) and of the rate constants ($k_3^f = 56 \pm 17 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_1^f = 0.025 \pm 0.001 \text{ s}^{-1}$) can be calculated. These values together with the rate constants for the second stage of the reaction (k_1^s and k_2^s) are also reported in Scheme 2.

A point that deserves to be underlined is the different reactivity of complex **1** with respect to that of the previously studied dichloro(pyridine-2-methanolato)gold(III)^[5] as regards the reaction with Cl^- in the absence of acid. In the first case no reaction takes place, whereas in the second case the reaction goes to completion with ring opening at oxygen followed by substitution of the pyridine ligand. This different behaviour, which implies a stronger Au–O bond in complex **1**, would suggest a remarkable effect on the reactivity as a result of the replacement of a hydrogen atom with a methoxy group, possibly related to their different inductive effects. Accordingly, both the values of the protonation constant ($K = 1.12 \text{ mol}^{-1} \text{ dm}^3$) and the rate con-

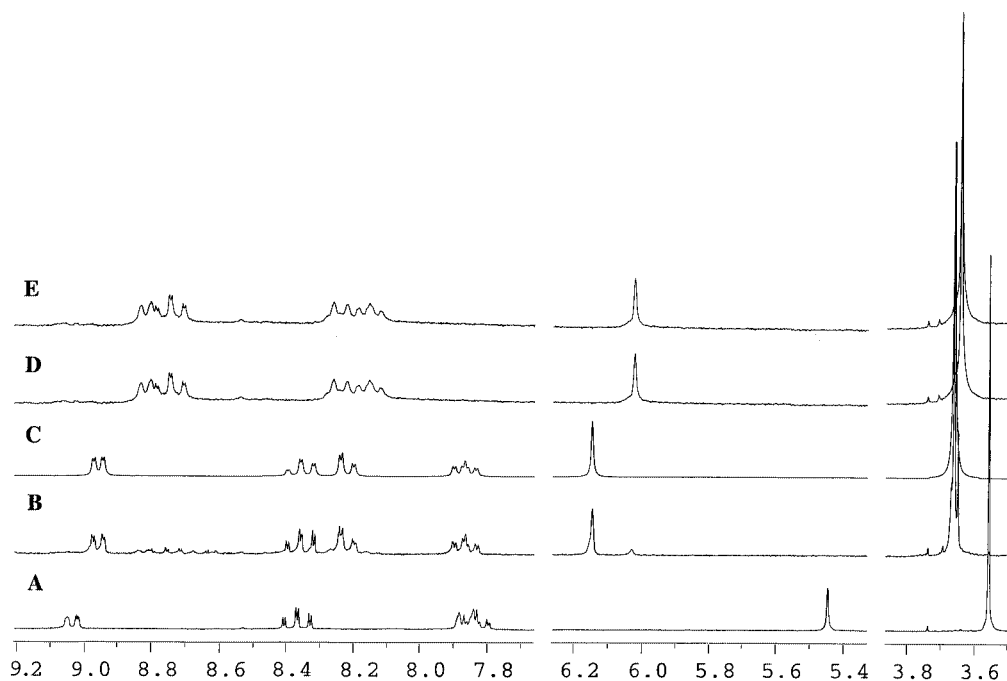


Figure 6. ^1H NMR spectrum of **1** in CD_3NO_2 (spectrum A); spectrum of **1** in methanol and DCl [molar ratio 5:1 and 1:1 with respect to the concentration of the complex] (spectrum B); spectrum of an authentic sample of **2** in CD_3NO_2 (spectrum C); spectrum of the released ligand at the end of the reaction in the presence of methanol and an excess of DCl [molar ratio 5:1 and 10:1 with respect to the concentration of complex (**1**)] (spectrum D); spectrum of the released ligand from **2** under the same experimental conditions (spectrum E).

$$k_{\text{obs}}^{\text{f}} = \frac{K[\text{H}^+]}{1 + K[\text{H}^+]} \left(\frac{k_1^{\text{f}} k_2^{\text{f}} [\text{Cl}^-]}{k_{-1}^{\text{f}} + k_2^{\text{f}} [\text{Cl}^-]} + k_3^{\text{f}} [\text{Cl}^-] \right) \quad (7)$$

$$k_{\text{obs}}^{\text{f}} = \frac{k_1^{\text{f}} K [\text{H}^+]}{1 + K [\text{H}^+]} + \frac{k_3^{\text{f}} K [\text{H}^+] [\text{Cl}^-]}{1 + K [\text{H}^+]} \quad (8)$$

stant relative to the ring opening of the protonated species ($k_3^{\text{f}} = 56 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) for the hemiacetalic complex (**1**) are lower than the corresponding constants for the complex with pyridine-2-methanol ($K = 9.7 \text{ mol}^{-1} \text{ dm}^3$, $k = 126 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$).^[5]

The second stage of the reaction, that is the displacement of the 2-substituted pyridine by Cl^- from the species **P'**, can be compared with other reactions of this sort as it is known that the second-order rate constant for the reaction with chloride depends upon the basicity of the leaving pyridine, according to the linear relationship $\log k_2 = a(\text{p}K_{\text{a}}) + C$ ($\text{p}K_{\text{a}}$ is that of the protonated base in water at 25°C) and is independent from steric hindrance of the ring substituents.^[7] In the mixture methanol/water (95:5, v/v) this relationship is also obeyed and the values of a and C , already measured, are -0.67 and 2.81 respectively.^[9] A k_2^{s} value of $7.6 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ leads therefore to a $\text{p}K_{\text{a}}$ of 5.86 for the leaving pyridine-2-carbaldehyde dimethyl acetal, which closely compares to those of pyridine-2-methanol and 2-(methoxymethyl)pyridine, as they both have a $\text{p}K_{\text{a}}$ value of 5.6 .^[5]

Concluding Remarks

The kinetics of ring opening and displacement of the bidentate chelate ligand from dichloro[pyridine-2-(α -methoxymethanolato)]gold(III), $[\text{Au}(\text{N}-\text{O})\text{Cl}_2]$ (**1**) have been studied spectrophotometrically in methanol/water (95:5 v/v). Because of the relative inertness of the Au-alkoxide oxygen bond, complex **1** does not react with chloride alone. In the presence of LiCl and perchloric acid the reaction proceeds through a pre-equilibrium protonation of the coordinated oxygen followed first by ring opening at oxygen accompanied by the entry of chloride or solvent and then by displacement of the *N*-bonded ligand to give $[\text{AuCl}_4]^-$. However, once opened the hemiacetalic *N*-coordinated ligand is rapidly transformed in the corresponding 2-(pyridinecarbaldehyde dimethyl acetal), which is the true leaving ligand, to be displaced in the second stage of the reaction as a 2-substituted pyridine with a $\text{p}K_{\text{a}}$ value of 5.86 .

Experimental Section

Materials: Pyridine-2-carbaldehyde (Aldrich) was vacuum distilled and stored at 4°C . Potassium tetrachloroaurate(III) dihydrate, the inorganic salts and the solvents were reagent grade products (Aldrich) used without further purification.

Instruments: UV/Vis spectra and kinetics were recorded with a Perkin-Elmer Lambda 5 spectrophotometer. IR spectra (4000 – 500 cm^{-1} , KBr disks; 600 – 50 cm^{-1} , polyethylene pellets) were collected with a Nicolet Magna FTIR 750 spectrometer. ^1H NMR spectra in high purity CD_3NO_2 (Aldrich) were obtained with a Bruker AC 200 spectrometer. Chemical shifts (ppm) were internally

referenced to the residual undeuterated solvent resonances and related to tetramethylsilane ($\delta = 0$ ppm). Conductivity measurements were carried out in dmf with a CDM 83 Radiometer Copenhagen conductivity meter and a CDC 334 immersion cell. Elemental analyses were performed by the Microanalytical Laboratory of the University of Padua.

Synthesis of Complexes 1 and 2 and of the Ligand Released at the End of the Process (3)

Dichloro[pyridine-2-(α -methoxymethanolato)]gold(III) (1): [Spectrum A in Figure 6] This complex was prepared following the same procedure as for the ethoxy species previously reported^[4] using methanol instead of ethanol as a solvent. Yield (80%). $\text{C}_7\text{H}_8\text{AuCl}_2\text{NO}_2$ (406.02): calcd. C 20.71, H 1.99, Cl 17.46, N 3.45; found C 20.64, H 1.72, Cl 17.32, N 3.46. ^1H NMR (200 MHz, CD_3NO_2 , 25 °C): $\delta = 9.04$ (d, $^3J_{\text{HH}} = 5.2$ Hz, 1 H, py- H_6), 8.37 (td, $^3J_{\text{HH}} = 7.6$, $^4J_{\text{HH}} = 1.4$ Hz, 1 H, py- H_4), 7.92–7.77 (m, 2 H, py- $\text{H}_{3,5}$), 5.45 (s, 1 H, CH), 3.56 (s, 3 H, OCH_3) ppm. Selected IR bands: 1609 ($\nu_{\text{C}=\text{N}}$), 1079 ($\nu_{\text{O}-\text{CH}_3}$), 370, 349 ($\nu_{\text{Au}-\text{Cl}}$) cm^{-1} . $A_{\text{M}}(\text{dmf}) = 2.7 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$.

Trichloro(pyridine-2-carbaldehyde dimethyl acetal)gold(III) (2): [Spectra B, C in Figure 6] The complex was prepared as previously reported.^[6] Yield (75%). $\text{C}_8\text{H}_{11}\text{AuCl}_3\text{NO}_2$ (456.51): calcd. C 21.05, H 2.43, Cl 23.30, N 3.07; found C 20.94, H 2.39, Cl 23.61, N 3.10. ^1H NMR (200 MHz, CD_3NO_2 , 25 °C): $\delta = 8.96$ (d, $^3J_{\text{HH}} = 6.0$ Hz, 1 H, py- H_6), 8.36 (td, $^3J_{\text{HH}} = 7.9$, $^4J_{\text{HH}} = 1.4$ Hz, 1 H, py- H_4), 8.22 (dd, $^3J_{\text{HH}} = 7.9$, $^4J_{\text{HH}} = 1.8$ Hz, 1 H, py- H_3); 7.87 (ddd, $^3J_{\text{HH}} = 6.0$, $^3J_{\text{HH}} = 7.9$, $^4J_{\text{HH}} = 1.8$ Hz, 1 H, py- H_5), 6.15 (s, 1 H, CH), 3.66 (s, 6 H, OMe_2) ppm. Selected IR bands: 1611 ($\nu_{\text{C}=\text{N}}$), 1098 ($\nu_{\text{O}-\text{CH}_3}$), 366, 349 ($\nu_{\text{Au}-\text{Cl}}$) cm^{-1} . $A_{\text{M}}(\text{dmf}) = 2.3 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$.

2-CH(OMe) $_2$ py-HCl (3): [Spectra D, E in Figure 6] ^1H NMR (200 MHz, CD_3NO_2 , 25 °C): $\delta = 8.81$ (d, $^3J_{\text{HH}} = 6.0$ Hz, 1 H, py- H_6), 8.75 (td, $^3J_{\text{HH}} = 7.9$, $^4J_{\text{HH}} = 1.6$ Hz, 1 H, py- H_4), 8.30–8.08 (m, 2 H, py- H_3+H_5), 6.91 (br, 1 H, NH), 6.02 (s, 1 H, CH), 3.64 (s, 6 H, OMe_2) ppm.

Kinetics: The reactions were followed spectrophotometrically by measuring the changing absorbance at a suitable wavelength as a

function of time. They were initiated by adding 10–20 μL of a 0.015 mol dm^{-3} dimethylformamide (dmf) solution of 1 or 2 to a methanol/water (95:5 v/v) solution (3 cm^3) of the appropriate reagent, either HClO_4 or HClO_4 , and LiCl, previously brought to the reaction temperature (25 °C) in the thermostatted cell in the spectrophotometer. All reactions were carried out at constant ionic strength ($I = 1.0 \text{ mol dm}^{-3}$, LiClO_4). Pseudo-first-order rate constants ($k_{\text{obs}}/\text{s}^{-1}$) were obtained either from the gradients of plots of $\log(D_t - D_\infty)$ versus time or from a nonlinear least-squares fit of experimental data to the equation $D_t = D_\infty + [D_0 - D_\infty \exp(-k_{\text{obs}}t)]$, where D_0 , D_∞ and k_{obs} are the parameters to be optimised (D_0 is absorbance after mixing of reactants, D_∞ is absorbance at completion of reaction). Rate constants were accurate within 5%.

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