Displacement of Chelate Ligands from Planar Four-co-ordinate Complexes. Part 5.[1] Preparation and Ligand-substitution Reaction of Dichloro(ethylenediamine)- and Dichloro(propylenediamine)-gold(III) Complexes

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The displacement of the chelate ligand (N–N) from the title complexes $[Au(en)Cl_2]^+$ and $[Au(pn)Cl_2]^+$ has been studied in a hydrochloric acid medium, $I = 1.7$ mol dm^{-3}, using aqueous methanol (95%) or water as solvent. The reaction takes place in two stages: an initial equilibrium between singly and doubly co-ordinate diamine is established, followed by displacement of the singly bonded protonated ligand from the metal. The rate constants for opening of the chelate ring and displacement of the half-detached ligand, and the quotient of the rate constant for ring closure and the basicity constant of the half-bonded diamine, have been determined. Comparison is made with data for displacement of analogous ligands from complexes of Pd^{II} and Pt^{II}.

In previous papers we reported the displacement of chelate *N*-donor ligands (N–N) from gold(III) complexes of formula $[AuX_2(N-N)]^+$ (X = halide).[1] With aliphatic amines (N–N = *NNN'N'*-tetramethylethylenediamine, *NNN'N'*-tetraethylethylenediamine, monoprotonated 3-azapentane-1,5-diamine, or monoprotonated 3-methyl-3-azapentane-1,5-diamine) a two-step reaction seemed to occur but we could only follow the kinetics of displacement of the protonated half-detached ligand from the central metal. From the experimental data the product of the equilibrium constants for reversible opening of the chelate ring and protonation of the free end of the singly bonded diamine was measured with good accuracy; the determination of the individual constants was, instead, doubtful. In order to obtain more information we have now extended the investigation to the complexes of ethylenediamine (en) and propylenediamine (pn). These complexes have been prepared for the first time and allow a comparison between the reactivity of five- and six-membered chelate rings.

EXPERIMENTAL

Hydrogen tetrachloroaurate(III) trihydrate was obtained from Johnson, Matthey and Co.; solvents, inorganic salts, ethylenediamine (en), and propylenediamine (pn) were all reagent-grade products.

Preparations.—Dichloro(*ethylenediamine*)*gold*(III) *chloride.* A solution of ethylenediamine in diethyl ether (0.076 g, 1.27 mmol in 20 cm^3) was added slowly, with stirring, to a

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[1] Part 4, G. Annibale, G. Natile, and L. Cattalini, *J.C.S. Dalton*, 1976, 1547.

solution of $HAuCl_4 \cdot 3H_2O$ in the same solvent (0.500 g, 1.27 mmol in 30 cm^3). A yellow crystalline compound immediately precipitated from the solution. The precipitate was dissolved in methanol (30 cm^3), treated with the stoicheiometric amount of lithium hydroxide (0.030 g, 1.27 mmol in 20 cm^3 of methanol, added dropwise over 2 h) and the solution left stirring overnight. The solution was then concentrated to 4—5 cm^3 under reduced pressure, cooled in an ice-bath, and filtered in order to remove a small amount of $[Au(en)_2]Cl_3$. The filtrate, treated with diethyl ether (20 cm^3), gave a pale yellow precipitate of the desired complex (0.37 g, 80% yield) {Found: C, 6.2; H, 2.6; Cl, 29.1; N, 7.2. $[AuCl_2(en)]Cl$ requires C, 6.6; H, 2.20; Cl, 29.25; N, 7.70%}.

The complex $[AuCl_2(pn)]Cl$ was prepared similarly {Found: C, 10.0; H, 2.9; Cl, 28.5; N, 7.7. $[AuCl_2(pn)]Cl$ requires C, 9.55; H, 2.65; Cl, 28.2; N, 7.40%}.

Kinetics.—Rate data were obtained spectrophotometrically by measuring changes of absorbance with time using an Optica CF4R double-beam instrument. Separate solutions of complex and reagents were prepared in methanol (containing 5% water) or water, brought to reaction temperature, and mixed in the thermostatted cell of the spectrophotometer. The concentrations of chloride and perchloric acid were checked by standard titrimetric methods. All the kinetic runs were performed in the presence of excesses of entering reagents and at constant ionic strength (1.7 mol dm^{-3}, $Li[ClO_4]$). The rate constant for the establishment of the equilibrium between the half- and fully co-ordinated diamine was measured either starting from $[AuCl_2(N-N)]^+$ and allowing it to react with excess of Cl^- and H^+, or starting from a solution of ten-fold higher concentrations of reagents and substrate in which the equilibrium had already been established and measuring, after dilution by a factor of 10, the rate of approach to the new equilibrium. Both methods gave the same value of $k_{obs.}$ for equal $[Cl^-]$ and $[H^+]$ in the final solution.

First-order rate constants were calculated from plots of $\ln(A_\infty - A_t)$ against time, where A_t and A_∞ are absorbances at time t and after at least six half-lives respectively. These plots were linear for at least four half-lives. The experimentally determined rate constants, k_{obs}/s^{-1}, are reported in Tables 1—5. The values of the intercepts and gradients of the linear plots were calculated from least-squares fits and the uncertainties quoted are 95% confidence limits.

RESULTS

The reaction of gold(III) halides with ethylenediamine and propylenediamine was investigated by Block and Bailar.[2] They produced evidence for the formation in solution of $[AuBr_2(N-N)]^+$; however all attempts to isolate this complex were unsuccessful, resulting always in the formation of the adduct containing two diamine molecules per atom of gold or in reduction to metal. To our knowledge, no reports on the isolation of a species containing one ligand molecule per atom of gold have appeared in the literature. We prepared such a species starting from $[HN-N][AuCl_4]$ dissolved in methanol and treated, slowly, with the stoicheiometric amount of lithium hydroxide. Using this procedure the 1 : 1 adduct is formed in high yield together with a small amount of bis(diamine) complex which, being far less soluble in this solvent, can be separated by reducing the solution to small volume and cooling to 0 °C. The desired product can then be precipitated from methanol by addition of diethyl ether.

The complexes $[AuCl_2(N-N)]^+$ (N–N = en or pn) react with hydrochloric acid to give, as final products, $[AuCl_4]^-$ and $[H_2N-N]^{2+}$. The spectroscopic course of the reaction is similar in both cases and that of the pn derivative is shown in Figure 1. The presence of an isosbestic point at the beginning indicates that only one process is taking place; however, as the reaction proceeds, this isosbestic is lost and simultaneously a new isosbestic appears at a different wavelength. The final spectrum corresponds to that of $[AuCl_4]^-$.[3] Therefore the displacement of the bidentate ligand occurs in two consecutive steps. In the first step one end of the ligand is displaced, and in the

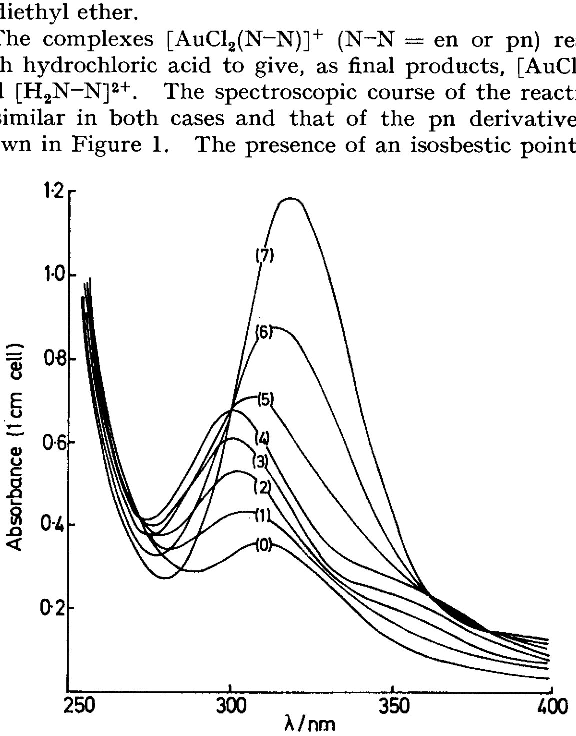

FIGURE 1 Spectroscopic course of the reaction $[AuCl_2(pn)]^+ + 2Cl^- + 2H^+ \longrightarrow [AuCl_4]^- + [H_2pn]^{2+}$ in aqueous methanol (95%). $[Complex]_0 = 2 \times 10^{-4}$, $[H^+] = 0.1$, $[Cl^-] = 0.34$, $I = 1.7$ mol dm^{-3} ($Li[ClO_4]$), 25 °C. Curves (0)—(7) show spectra at zero time and after 0.8, 1.75, 3.08, 12, 35, 105, and 720 min respectively

TABLE 1

Values of $k_{obs.}$ for the reaction $[AuCl_2(pn)]^+ \longrightarrow [AuCl_3(Hpn)]^+$ in aqueous methanol (95%) at $I = 1.7$ mol dm^{-3} ($Li[ClO_4]$) and 25 °C

$\frac{10^2[Cl^-]}{mol\ dm^{-3}}$	$\frac{10^2[H^+]}{mol\ dm^{-3}}$	$\frac{10^3\ k_{obs.}}{s^{-1}}$
2.32	0.64	1.90
2.32	0.73	1.73
2.32	0.91	1.54
2.32	1.36	1.23
2.32	1.82	1.06
2.32	2.73	0.89
2.32	4.50	0.76
2.32	98.6	0.60
11.3	46.7	2.46
22.7	46.7	5.01
34.0	46.7	7.20
44.0	46.7	9.39
55.3	46.7	12.1
66.7	46.7	14.0

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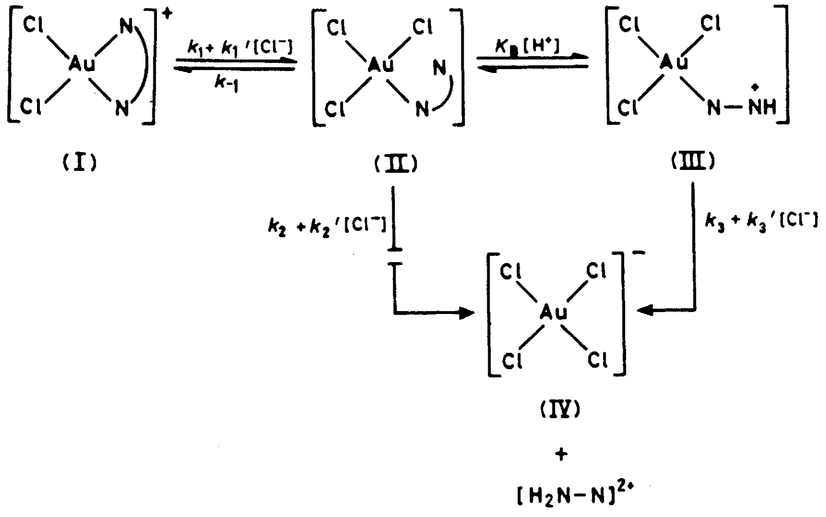
[2] B. P. Block and C. Bailar, jun., *J. Amer. Chem. Soc.*, 1951, **73**, 4722.

[3] H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, 1963, **85**, 260; A. K. Gongopadhayay and A. Chakzavorty, *J. Chem. Phys.*, 1961, **35**, 2206.

second step the singly bonded diamine is displaced. The absorbance and wavelength of the second isosbestic varied with the chloride- and hydrogen-ion concentrations indicating that the first step of the reaction is an equilibrium. The rate of establishment of this equilibrium was measured from the changes of absorbance with time at the wavelength of the second isosbestic point.



SCHEME

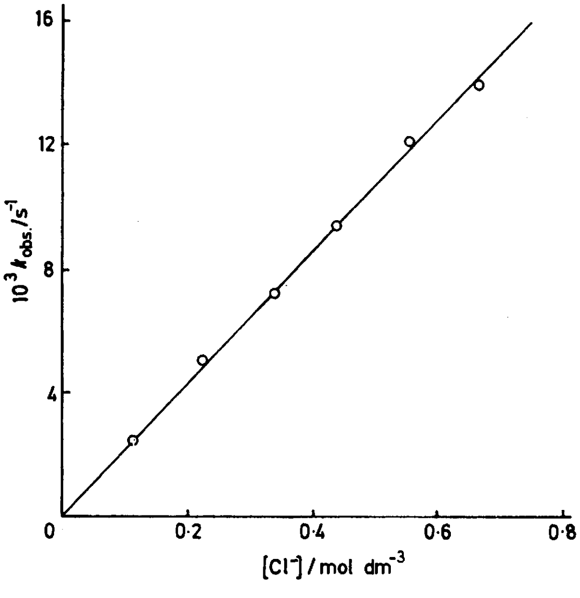


FIGURE 2 Dependence of $k_{obs.}$ on $[Cl^-]$ for the reaction $[AuCl_2(pn)]^+ \longrightarrow [AuCl_3(Hpn)]^+$ in aqueous methanol (95%) at $[H^+] = 0.47$, $I = 1.7\ mol\ dm^{-3}$ ($Li[ClO_4]$), and 25 °C

Opening of the Chelate Ring in $[AuCl_2(pn)]^+$.—The observed rate constants in aqueous methanol (95%) are given in Table 1. At a given hydrogen-ion concentration a plot of $k_{obs.}$ against $[Cl^-]$ was linear (Figure 2). Keeping

$$k_{obs.} = k_1 + k_1'[Cl^-] + \frac{k_{-1}}{1 + K_B[H^+]} \qquad (1)$$

$[Cl^-]$ constant and increasing $[H^+]$, $k_{obs.}$ decreased to a limiting value and a plot of $k_{obs.}$ against $1/[H^+]$ was also linear (Figure 3). Both these results are in accord with the reactions in the first line of the Scheme, from which equation (1) can be deduced for the dependence of $k_{obs.}$ on $[H^+]$ and $[Cl^-]$. A plot of $k_{obs.}$ against $[Cl^-]$ at constant $[H^+]$ had a nearly zero intercept and we conclude that k_1 is small; the gradient of this plot gives k_1'.

According to equation (1) the intercept of the linear plot of $k_{obs.}$ against $1/[H^+]$ at constant $[Cl^-]$ is $(k_1 + k_1'[Cl^-])$; subtracting $k_1'[Cl^-]$ (calculated from the value of k_1' previously obtained) from this intercept gave an estimate of k_1. The gradient of this plot gave k_{-1}/K_B; in fact, since $k_{obs.}$ is proportional to $1/[H^+]$, it follows that $K_B[H^+] \gg 1$.

The same reaction was studied in water. The observed spectral changes were similar and the measured rate constants are in Table 2. At constant $[H^+]$, $k_{obs.}$ was a linear function of $[Cl^-]$ and according to equation (1) the gradient of a plot of $k_{obs.}$ against $[Cl^-]$ gave k_1' and the intercept

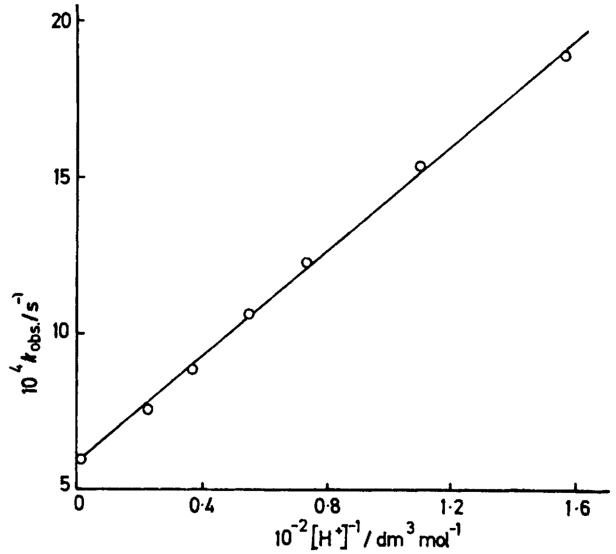


FIGURE 3 Dependence of $k_{obs.}$ on $1/[H^+]$ for the reaction $[AuCl_2(pn)]^+ \longrightarrow [AuCl_3(Hpn)]^+$ in aqueous methanol (95%) at $[Cl^-] = 0.023$, $I = 1.7\ mol\ dm^{-3}$ ($Li[ClO_4]$), and 25 °C

$k_1 + k_{-1}/(1 + K_B[H^+])$. The presence of a discrete intercept in this diagram did not allow us to draw any conclusion as to the relative magnitude of k_1 and k_1'. However, from the plot of $k_{obs.}$ against $1/[H^+]$ at constant $[Cl^-]$ we could determine $k_1 + k_1'[Cl^-]$ (intercept) and comparing this value with $k_1'[Cl^-]$ derived from the gradient of the former diagram we could estimate k_1. Also in this case, $K_B[H^+] \gg 1$ and the gradient of the linear plot gave k_{-1}/K_B.

TABLE 2

Values of $k_{obs.}$ for the reaction $[AuCl_2(pn)]^+ \longrightarrow [AuCl_3(Hpn)]^+$ in water at $I = 1.7$ mol dm^{-3} (Li[ClO$_4$]) and 25 °C

$10^2[Cl^-]$ / mol dm^{-3}	$10^2[H^+]$ / mol dm^{-3}	$10^3 k_{obs.}$ / s^{-1}
7.02	60.0	0.23
17.1	60.0	0.39
34.0	60.0	0.64
51.0	60.0	0.90
68.2	60.0	1.16
93.1	60.0	1.54
34.0	2.00	2.78
34.0	3.00	2.03
34.0	4.00	1.65
34.0	6.00	1.35
34.0	8.00	1.19
34.0	10.0	1.06
34.0	14.0	0.93
34.0	20.0	0.83
34.0	30.0	0.74

TABLE 3

Values of $k_{obs.}$ for the reaction $[AuCl_2(en)]^+ \longrightarrow [AuCl_3(Hen)]^+$ in aqueous methanol (95%) at $I = 1.7$ mol dm^{-3} (Li[ClO$_4$]) and 25 °C

$10^2[Cl^-]$ / mol dm^{-3}	$10^2[H^+]$ / mol dm^{-3}	$10^3 k_{obs.}$ / s^{-1}
6.51	46.5	2.89
13.3	46.5	3.50
27.7	46.5	5.42
34.0	46.5	7.07
39.2	46.5	8.06
44.0	46.5	8.58
52.3	46.5	9.95
56.7	46.5	10.8
66.7	46.5	12.5
77.0	46.5	13.8
22.7	20.0	7.38
22.7	33.3	6.13
22.7	46.7	5.42
22.7	53.3	5.24
26.2	7.70	13.2
26.2	15.4	8.79
26.2	61.5	5.61

The value of k_1 plus the term $k_{-1}/K_B[H^+]$ should account for the whole intercept observed in the plot of $k_{obs.}$ against $[Cl^-]$ at constant $[H^+]$. In fact the calculated value of $(1.74 \pm 0.35) \times 10^{-4}$ s^{-1} agrees, within the limits of the experimental error, with that of the intercept, $(1.26 \pm 0.1) \times 10^{-4}$ s^{-1}.

Opening of the Chelate Ring in $[AuCl_2(en)]^+$.—The spectroscopic course of this reaction in aqueous methanol is similar to that observed with the analogous pn complex; however, in this case the equilibrium between the singly and doubly co-ordinated diamine is more shifted towards the latter chelate form, and consequently the observed spectral changes were smaller. The observed rate constants are given in Table 3.

At constant acid concentration the reaction rate was a linear function of $[Cl^-]$ and according to equation (1) the gradient of a plot of $k_{obs.}$ against $[Cl^-]$ gave k_1'.

A plot of $k_{obs.}$ against $1/[H^+]$ at constant $[Cl^-]$ was also linear, the gradient being k_{-1}/K_B; from the intercept, by subtracting $k_1'[Cl^-]$ calculated assuming the value of k_1' determined from the previous plot, we calculated k_1 which, once again, appeared to be small compared with k_1'.

Displacement of Singly Bonded Propylenediamine.—The experimental rate constants are given in Table 4. At a given chloride concentration the reaction rate did not vary significantly on varying the concentration of acid by a factor of 15. On the other hand, when the concentration of acid was held constant and the concentration of chloride varied the reaction rate varied linearly. These results indicate that under experimental conditions ($[Cl^-] = 0.68$, $[H^+] \geqslant 0.04$; or $[H^+] = 0.04$, $[Cl^-] \geqslant 0.10$ mol dm^{-3}) the equilibria (I) $\rightleftharpoons$ (II) $\rightleftharpoons$ (III) (see Scheme) are completely shifted in favour of (III), therefore the reaction rate does not depend on $[H^+]$.

TABLE 4

Values of $k_{obs.}$ for the reaction $[AuCl_2(pn)]^+ \longrightarrow [AuCl_4]^-$ in aqueous methanol (95%), at $I = 1.7$ mol dm^{-3} (Li[ClO$_4$]) and 25 °C

$10^2[Cl^-]$ / mol dm^{-3}	$10^2[H^+]$ / mol dm^{-3}	$10^4 k_{obs.}$ / s^{-1}
68.1	4.02	2.68
68.1	8.01	2.66
68.1	20.2	2.65
68.1	40.2	2.65
68.1	60.0	2.66
34.0	20.2	1.40
85.1	20.2	3.33
120.0	20.2	4.73

The gradient of a linear plot of $k_{obs.}$ against $[Cl^-]$ gave k_3', and since the intercept appeared to be zero we concluded that k_3 is small compared with k_3'.

TABLE 5

Values of $k_{obs.}$ for the reaction $[AuCl_2(en)]^+ \longrightarrow [AuCl_4]^-$ at constant $[Cl^-]$ and variable $[H^+]$, $I = 1.7$ mol dm^{-3} (Li[ClO$_4$]), and 25 °C

$10^2[Cl^-]$ / mol dm^{-3}	$10^2[H^+]$ / mol dm^{-3}	$10^4 k_{obs.}$ / s^{-1}
17.0	8.0	2.28
	12.0	2.97
	20.0	3.94
	60.0	5.95
	80.0	6.54
30.9	3.64	3.35
	5.45	4.44
	10.9	6.64
	18.2	8.47
	54.5	11.0
61.8	1.80	6.73
	3.64	10.7
	5.45	13.3
	18.2	20.8
	54.5	25.9
93.0	1.80	14.3
	3.60	20.3
	7.30	28.0
	18.2	35.1
	36.4	38.5

Displacement of Singly Bonded Ethylenediamine.—The observed rate constants are given in Table 5. At a given chloride concentration the reaction rate increased with increasing acid concentration to a limiting value at high

[H$^+$]. Plotting the reciprocal of the rate constant against the reciprocal of the acid concentration gave a straight line having intercept B_0 and gradient B_1 [equation (2)]. The

$$k_{\text{obs.}} = [\text{H}^+]/(B_0[\text{H}^+] + B_1) \qquad (2)$$

TABLE 6

Values of the intercepts, B_0 (at $1/[\text{H}^+] = 0$), and gradients, B_1, of straight lines obtained from plots of $1/k_{\text{obs.}}$ against $1/[\text{H}^+]$ at constant [Cl$^-$] using the values listed in Table 5

$\dfrac{[\text{Cl}^-]}{\text{mol dm}^{-3}}$	$\dfrac{10^{-2}B_0}{\text{s}}$	$\dfrac{10\,B_1}{\text{mol dm}^{-3}\text{ s}}$
0.17	12.48 ± 0.73	25.25 ± 1.02
0.31	7.52 ± 0.34	8.13 ± 0.22
0.62	3.63 ± 0.26	2.05 ± 0.09
0.93	2.42 ± 0.25	0.85 ± 0.09

values of B_0 and B_1 calculated by least-squares fits are given in Table 6. A plot of $1/B_0$ against [Cl$^-$] was linear and passed through the origin [intercept $9 \times 10^{-6} \pm 1.9 \times 10^{-4}$, gradient $(4.43 \pm 0.23) \times 10^{-3}$] according to equation (3). Also a plot of B_1[Cl$^-$] against 1/[Cl$^-$] gave

$$B_0 = r/[\text{Cl}^-] \qquad (3)$$

a straight line with zero intercept 0.79 ± 3.47 and gradient 7.24 ± 0.47 according to equation (4).

$$B_1 = s/[\text{Cl}^-]^2 \qquad (4)$$

From equations (2)—(4) expression (5) is deduced for the overall dependence of $k_{\text{obs.}}$ on [H$^+$] and [Cl$^-$]. The absence

$$k_{\text{obs.}} = \frac{[\text{H}^+][\text{Cl}^-]^2}{r[\text{H}^+][\text{Cl}^-] + s} \qquad (5)$$

of an additional term independent of [H$^+$] in the numerator of equation (5) allows us to assume that the contribution of ($k_2 + k_2'[\text{Cl}^-]$) (see Scheme) to the reaction rate is negligible: moreover, from the kinetics of approach to the equilibrium (I) $\rightleftharpoons$ (III) it has been shown that k_1 can also be neglected as an additional term with respect to $k_1'[\text{Cl}^-]$. Therefore, making these approximations, equation (6) can be deduced from the Scheme for the complete displacement of the chelate ligand from the metal. Com-

$$k_{\text{obs.}} = \frac{k_1'[\text{Cl}^-](k_3 + k_3'[\text{Cl}^-])K_{\text{B}}[\text{H}^+]}{k_{-1} + k_1'[\text{Cl}^-] + k_1'K_{\text{B}}[\text{Cl}^-][\text{H}^+]} \qquad (6)$$

paring equations (5) and (6) it follows that $k_3 \simeq 0$, $s = k_{-1}/k_1'k_3'K_{\text{B}}$, and $r = 1/k_3'$. It is to be noted that if $k_1'[\text{Cl}^-]$ were not negligible as an additional term in the denominator of equation (6) the linear plot of B_1[Cl$^-$] against 1/[Cl$^-$] would have had a discrete intercept. From the value of s, knowing k_1' and k_3', the quotient k_{-1}/K_{B} was calculated and found to agree satisfactorily with the value obtained independently from the kinetics of establishment of the equilibrium between species (I) and (III).

DISCUSSION

The adopted reaction scheme accounts satisfactorily for the occurrence of a delayed isosbestic point whose wavelength and absorbance change with the acid and chloride concentrations, and for the quantitative dependence of the observed rate constants on the acid and chloride concentrations. By applying the standard formulae[4] for reversible reactions between species (I) and (III) equation (1) was deduced for the first stage of the reaction (that is until the delayed isosbestic appears), and from the experimental data the constants k_1, k_1', and k_{-1}/K_{B} were determined. Making the approximation of a pre-equilibrium between species (I) and (III) equation (6) was deduced for the conversion of (III) into (IV) (second stage of the reaction) and from the kinetic data the constants k_3' and $K_{\text{B}}k_1'k_3'/k_{-1}$ (the latter only for the en complex) were evaluated.

TABLE 7

Values of constants in equations (1) (first step) and (6) (second step) derived (see text) from results in Tables 1—5

	[AuCl$_2$(pn)]$^+$ Aqueous methanol	[AuCl$_2$(pn)]$^+$ Water	[AuCl$_2$(en)]$^+$ (aqueous methanol)
$10^4\,k_1/\text{s}^{-1}$	1.0 ± 0.5	1.0 ± 0.4	4.4 ± 2.1
$10^2\,k_1'/\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}$	2.1 ± 0.1	0.152 ± 0.002	1.58 ± 0.04
$10^5\,\dfrac{k_{-1}}{K_{\text{B}}}\Big/\text{mol dm}^{-3}\text{ s}^{-1}$	0.85 ± 0.03	0.43 ± 0.01	66.4 ± 1.9 (51 ± 14)*
$10^3\,k_3'/\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}$	0.39 ± 0.03		4.4 ± 0.2

* The value in parentheses was calculated from equation (6), whereas the other value was obtained from equation (1).

Steps (I) $\longrightarrow$ (II) and (III) $\longrightarrow$ (IV) were written in the general form for substitution reactions of square-planar complexes. However, comparing the solvolysis rate constant with the second-order rate constant it appears that Cl$^-$ is a much better entering group than the solvent, according to results previously reported for the displacement of nitrogen bases from gold(III) complexes.[5] A direct comparison between the k_1' values and the rate of substitution of the first amine from complexes of the type *cis*-[Au(amine)$_2$Cl$_2$]$^+$ would show whether some special feature is associated with the breaking of a chelate ring. To our knowledge such data are not available, neither can we make a comparison with data relative to the displacement of the base from [Au(amine)Cl$_3$] complexes since, among other things, the charge of the substrates is different and this can affect considerably the rate of displacement. The difference (factor of 14) between the k_1' values obtained in aqueous methanol and water for the [AuCl$_2$(pn)]$^+$ complex also indicates that charge neutralization and consequent desolvation of the reacting species in the formation of the transition state has a relevant effect on the reaction rate.

The rate constant for opening of the chelate ring (k_1') is of the same order of magnitude for both the en and pn substrates (1.6×10^{-2} and 2.1×10^{-2} dm^3 mol^{-1} s^{-1} respectively). It seems that the chelate-ring size has no effect on the rate of ring opening; however, in these complexes the effect of the different ring sizes could be balanced by the different basicities of the two diamines. In fact the *cis* effect and the leaving-group effect would favour ring opening in the en complex.[5,6]

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[4] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanisms,' 2nd edn., Wiley, New York, 1961, p. 186.

[5] L. Cattalini and M. L. Tobe, *Inorg. Chem.*, 1966, **5**, 1145; L. Cattalini, A. A. Orio, and M. L. Tobe, *ibid.*, 1967, **6**, 75.

[6] P. D. Braddock, R. Romeo, and M. L. Tobe, *Inorg. Chem.*, 1974, **13**, 1170.

The influence of the basicity of the leaving group on the rate of displacement appears clear when we compare the values of k_3' relative to the en and pn complexes (4.4×10^{-3} and 3.9×10^{-4} dm^3 mol^{-1} s^{-1} respectively. This relevant difference can only reflect the different basicity of $[\mathrm{Hen}]^+$ and $[\mathrm{Hpn}]^+$ (log K_B 7.74 and 9.03 respectively).[7] Extrapolated values of the rate constants obtained from a plot of log k against log K_B for the displacement of heterocyclic amines from the complexes $[\mathrm{Au(amine)Cl_3}]$ are 1.1×10^{-2} and 9.1×10^{-4} dm^3 mol^{-1} s^{-1} for log K_B 7.74 and 9.03 respectively. The discrepancy (factor of 2) between these calculated values and the experimental ones is small if we consider that no correction for the different steric hindrance of the amines has been made.

The measured value of k_{-1}/K_B is 6.6×10^{-4} and 8.5×10^{-6} mol dm^{-3} s^{-1} for the en and pn derivative respectively. These values can be compared with those obtained for a palladium complex [reaction (7), k_{-1}/K_B 2.5×10^{-4} mol dm^{-3} s^{-1}] [8] and for some platinum complexes [reactions (8), (9), and (10); k_{-1}/K_B 7.7×10^{-9}, 5.2×10^{-9}, and 1.5×10^{-4} mol dm^{-3} s^{-1} respectively].[9-11]

$$[\mathrm{Pd(en)_2}]^{2+} \underset{k_{-1}}{\rightleftharpoons} [\mathrm{Pd(en)(en')Cl}]^{+} \overset{K_\mathrm{B}[\mathrm{H}^+]}{\rightleftharpoons} [\mathrm{Pd(en)(Hen)Cl}]^{2+} \quad (7)$$

$$[\mathrm{Pt(en)(Hen)Cl}]^{2+} \underset{K_\mathrm{B}[\mathrm{H}^+]}{\rightleftharpoons} [\mathrm{Pt(en)(en')Cl}]^{+} \overset{k_{-1}}{\rightleftharpoons} [\mathrm{Pt(en)_2}]^{2+} \quad (8)$$

$$[\mathrm{Pt(3NMe\text{-}Hpd)Cl_2}]^{+} \underset{K_\mathrm{B}[\mathrm{H}^+]}{\rightleftharpoons} [\mathrm{Pt(3NMe\text{-}pd')Cl_2}] \overset{k_{-1}}{\rightleftharpoons} [\mathrm{Pt(3NMe\text{-}pd)Cl}]^{+} \quad (9)$$

$$[\mathrm{Pt(dmso)(en)Cl}]^{+} \underset{k_{-1}}{\rightleftharpoons} [\mathrm{Pt(dmso)(en')Cl_2}] \overset{K_\mathrm{B}[\mathrm{H}^+]}{\rightleftharpoons} [\mathrm{Pt(dmso)(Hen)Cl_2}]^{+} \quad (10)$$

Here en′ denotes unidentate unprotonated ethylenediamine, 3NMe-pd′ = bidentate unprotonated 3-methyl-3-azapentane-1,5-diamine, and dmso = dimethyl sulphoxide. For reaction (7), assuming $K_\mathrm{B} = 10^4$—10^5 dm^3 mol^{-1}, k_{-1} was evaluated as 2—20 s^{-1}.[8] For reactions (8) and (9), experimental values of k_{-1} (0.73 and 2.1 s^{-1} respectively) being available, it was possible to estimate K_B as 9.1×10^7 and 4×10^8 dm^3 mol^{-1} respectively, quite similar to the value for the second protonation of the ligand. By analogy with the two previous cases, a value of K_B of 10^8 dm^3 mol^{-1} was assumed for reaction (10) and consequently k_{-1} was estimated as 1.5×10^4 s^{-1}.

For the gold complexes we have also only the quotient k_{-1}/K_B and can evaluate one of these two constants only by assuming a value for the other. If we regard K_B as the protonation constant of a truly free end of a diamine which is bonded to a metal ion through the second end we can expect it not to vary much from case to case and to be quite similar to the second protonation constant of the free ligand; therefore we can assume for K_B the values of *ca.* 10^8 and 10^9 dm^3 mol^{-1} for en and pn respectively, and consequently we obtain $k_{-1} = 7 \times 10^4$ and 8×10^3 s^{-1}. These values suggest a greater ease of formation of a five- than a six-membered ring; in fact the *cis* effect of the first co-ordinated end of the diamine should not be much different in the two cases since the two amines have similar K_B values for the first protonation (log K_B 10.9 and 10.7 for pn and en respectively). On the other hand the entering-group effect should favour the more basic second end of pn over en.[12]

The values of k_{-1} are much larger than those found in reactions (8) and (9) and reflect the higher reactivity of the gold(III) substrates compared with those of Pt$^{\mathrm{II}}$, as found for the replacement of unidentate ligands.[13] The fact that in reaction (10) the k_{-1} value is unusually high and similar to those found for the gold(III) complexes is due to the high *trans* effect exerted by the dimethyl sulphoxide ligand in that platinum substrate.

In conclusion, from the values of k_1' and k_{-1} in the en and pn complexes it appears that the rates of ring opening and closing are affected by the ring size and that in the five-membered ring the closing process is easier and the breaking more difficult than in the six-membered ring. We have also seen from the values of k_3' that the rate of displacement of half-detached diamines is similar to that of unidentate amines once allowance is made for the different basicity of the leaving group. Comparison of the data in aqueous methanol and water for the pn complex also shows the influence of solvent on the rate of opening of the chelate ring (k_1'), as expected for a bimolecular process in which bond making and consequent desolvation of the reacting species dominates the activation energy.

As a final point we comment on the assumption that a singly co-ordinated diamine has a base strength similar to that of the monoprotonated form. Although this assumption is supported by experimental evidence,[9,10] it holds if there is no interaction between the free end of the half-detached diamine and the metal ion as expected for this type of amine in aqueous solvents. However, with different amines and/or other solvents the situation could be quite different. Although the planar geometry about the metal atom is strongly preferred in gold(III) complexes, solution and *X*-ray data have shown that five- and six-co-ordination can also occur.[14] In

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particular, complexes of type $[AuX_3(N-N)]$ (X = Cl or Br; N–N = biquinolyl or 2,9-dimethyl-1,10-phenanthroline)[15] have been isolated in the solid and their crystal structure has shown them to be square pyramidal with the bidentate ligand bridging one equatorial and one axial position; this configuration is also kept in solution in polar solvents such as nitrobenzene.

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