The Appearance of a Stable Intermediate in some Substitution Reactions of (1,5-Diamino-3-azapentane)pyridinepalladium(II) Perchlorate

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The kinetics and equilibria of the reversible displacement of pyridine (py) from $[Pd(dien)(py)]^{2+}$ (dien = 1,5-diamino-3-azapentane) in aqueous solution have been studied. In acidic solution the reaction is reversible and the solvolytic rate constant = $(2.5 \pm 0.1) \times 10^{-3}\ s^{-1}$ at 25 °C is independent of $[H^+]$. In the presence of excess of hydroxide the reaction goes to completion and the $[OH^-]$ dependence takes the form $10^3k_{obs.} = (2.33 \pm 0.1) + (6.3 \pm 0.8)[OH^-] + (8.05 \pm 0.9)[OH^-]^2\ s^{-1}$ at 25 °C, $I = 1.0$ mol dm^{-3}. Chloride ions interact readily with the complex but the change in absorbance, while qualitatively consistent with the displacement of pyridine by Cl^-, can only be accounted for if an intermediate species containing both chloride and pyridine is formed in significant quantity. The kinetics and equilibria of the formation of this species have been studied in neutral aqueous solution at 25 °C, $I = 1.0$ mol dm^{-3}. The nature of this intermediate is discussed.

With very few exceptions, the ligand substitution reactions of four-co-ordinate planar d^8 metal ion complexes are associatively activated[1,2] and frequently characterized by an *A* mechanism[3] in which the existence of a five-co-ordinate intermediate is postulated to account for a wide range of structure–activity relationships in terms of bond-making and bond-breaking aspects of the ligand substitution process. Occasionally, stable five-co-ordinate species can be isolated and characterized[4] but a disturbance of the kinetics of substitution owing to the formation of a metastable intermediate in the course of the reaction is a much rarer occurrence. It was suggested that the spectrophotometric changes associated with the displacement of $SbPh_3$ from $[Rh(cod)(SbPh_3)Cl]$ (cod = cyclo-octa-1,5-diene) by amines[5] were due to the rapid and reversible formation of significant quantities of the five-co-ordinate intermediate and the slow rate-determining loss of stibine that followed.

In the course of our extensive studies of the reactions of dicationic complexes of Pt^{II} we observed anomalies in the reactions of $[Pd(dien)(py)]^{2+}$ (dien = 1,5-diamino-3-azapentane, py = pyridine) with Cl^- that were reminiscent of those reported by Coe and Lyons[6] in studies of the analogous reactions of $[Pd(dien)(NH_3)]^{2+}$ and in this paper we report the results of our investigation.

Experimental

(i) *Compounds and Reagents.*—(1,5-*Diamino*-3-*azapentane*)-*pyridinepalladium*(II) *perchlorate.* Two molar equivalents of silver perchlorate were added to an ethanolic solution of [Pd(dien)Br]Br, prepared by the method of Baddley and Basolo,[7] and the solution was filtered from the precipitated AgBr. Slightly more than an equimolar amount of pyridine was added and the solution was evaporated to small volume. On the addition of a few drops of a concentrated solution of $LiClO_4$ in ethanol, white crystals separated and were filtered off and recrystallized from hot ethanol (Found: C, 21.85; H, 3.65; N, 11.30. $C_9H_{18}Cl_2N_4O_8Pd$ requires C, 22.15; H, 3.70; N, 11.5%).

The complex $[Pd(dien)Cl]^+$ was prepared in aqueous solution by adding 2 molar equivalents of $AgClO_4$ to a solution of [Pd(dien)Br]Br, filtering off the AgBr, and then adding an excess of NaCl.

All other reagents were either AR grade or else of the highest grade available.

(ii) *Kinetics and Equilibria.*—The reactions were initiated by mixing a freshly made solution of the complex in pre-thermostatted water with an equal volume of one containing all the other reagents previously brought to the reaction temperature. The subsequent reactions were followed spectrophotometrically using a Perkin-Elmer Lambda 5 spectrophotometer in the repetitive scanning mode (220—350 nm), if the reactions were slow enough, or by following the absorbance at a selected wavelength as a function of time. The equilibrium measurements were made using the spectra recorded when the reactions were complete.

Ionic strength was kept constant using sodium perchlorate.

^1H N.m.r. spectra of D_2O solutions of the complex were measured with a Varian FT 400 MHz spectrometer.

(iii) *Statistical Data Treatment.*—(a) *Kinetics: Analysis of absorbance* (A) vs. *time* (t) *data.* For most kinetic runs conforming to the customary monoexponential first-order decay, an infinite time measurement (A_∞) could be determined directly; however, an iterative non-linear least-squares program was employed to determine the values of $k_{obs.}$, A_0, and A_∞ which best fit the A_t *vs.* t data within the first-order rate expression $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs.}t)$, the function minimized being $\Sigma_i(A_{calc.} - A_{obs.})^2$. The algorithm employs a non-linear optimization procedure and converges in a few cycles from an estimated starting vector of parameters. To maintain internal consistency, all kinetic data were treated by this non-linear technique; where direct comparison was feasible, the optimized values of A_0 and A_∞ agreed with the observed values to well within experimental error. Within each experiment, the values of A_t calculated from the expression above and the optimized values of A_0, A_∞, and $k_{obs.}$ always agreed with the observed values of A_t to a standard deviation of less than 0.002 absorbance unit and on the average to a standard deviation of less than 0.001 absorbance unit. Residuals were randomly scattered and never greater than 0.0015 absorbance unit in absolute value. Estimated standard errors for $k_{obs.}$ were

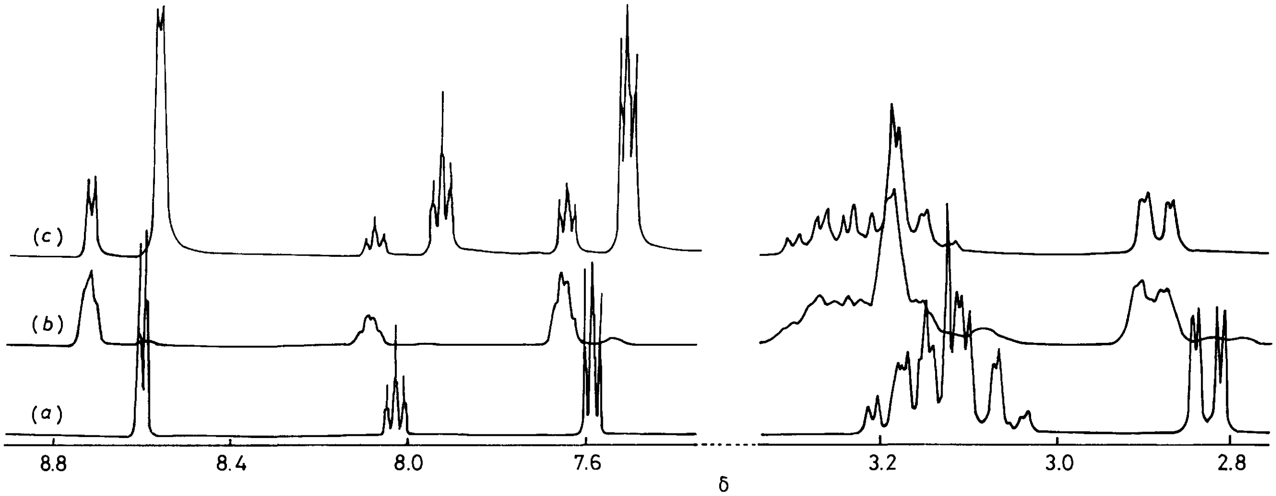


Figure 1. ^1H N.m.r. spectra of solutions of [Pd(dien)(py)][ClO$_4$]$_2$ (1.6×10^{-2} mol dm^{-3}) in (*a*) D_2O, (*b*) D_2O with added NaCl (5 mol dm^{-3}), and (*c*) D_2O with added NaCl (5 mol dm^{-3}) and excess of free pyridine (5×10^{-2} mol dm^{-3})

determined from the corresponding diagonal element of the variance/covariance matrix of parameters estimated at convergence of the non-linear least-squares fitting. Uncertainties quoted are one standard error of estimate.

(b) *Equilibria: Analysis of absorbance* (A) vs. *concentration data.* Absorbance *vs.* concentration data for equilibrium studies were similarly analysed by a non-linear optimization procedure based on models to be described under Results. Uncertainties quoted for equilibrium constants are one standard error of estimate.

Results

(i) *The Reversible Displacement of Pyridine from* [Pd(dien)(py)]$^{2+}$ *in Acidic Solution.*—(a) *Equilibria.* Aqueous solutions of [Pd(dien)(py)][ClO$_4$]$_2$ are stable for long periods. The ^1H n.m.r. spectrum of a 10^{-2} mol dm^{-3} solution in D_2O shows the characteristic three multiplets for co-ordinated pyridine at δ 8.60 [d of d, $H^{2,6}$, 2 H, $^3J(H^2H^3) = {}^3J(H^6H^5) = 6.5$, $^4J(H^2H^4) = {}^4J(H^6H^4) = 1.6$ Hz, 8.03 [t of t, H^4, 1 H, $^3J(H^4H^3) = {}^3J(H^4H^5) = 7.8$, $^4J(H^4H^2) = {}^4J(H^4H^6) = 1.6$ Hz], and 7.59 (m, $H^{3,5}$, 2 H) and the signals for the dien C–H protons appear as an ABCX multiplet with 'X' (not assigned) at δ 2.85 [d of d, dien $H_\alpha H_{\alpha'}$, 2 H, $^3J(H_\alpha H_\beta) = {}^3J(H_{\alpha'} H_{\beta'}) = 11.5$, $^3J(H_\alpha H_\gamma) = {}^3J(H_{\alpha'} H_{\gamma'}) = 3.5$ Hz] and a complex multiple signal around δ 3.12 (6 H) (Figure 1). The amine protons exchange rapidly with solvent and do not appear. On adding excess of perchloric acid the original pyridine protons decrease in intensity and a new set, assigned to Hpy$^+$, appear. The spectra are consistent with the distribution of the pyridine between two sites with no site exchange on the n.m.r. time-scale. The observed process therefore corresponds to equations (1) and (2).

$$[\mathrm{Pd(dien)(py)}]^{2+} + H_3O^+ \underset{}{\overset{K_{tot.}}{\rightleftharpoons}} [\mathrm{Pd(dien)}(H_2O)]^{2+} + \mathrm{Hpy}^+ \quad (1)$$

$$\mathrm{Hpy}^+ + H_2O \overset{K_a}{\rightleftharpoons} \mathrm{py} + H_3O^+ \quad (2)$$

Using more dilute solutions of the complex (*ca.* 10^{-4} mol dm^{-3}), equilibrium (1) was studied spectrophotometrically. The absorbance *vs.* $[H^+]_{tot.}$ data were fitted by the equation using the independently determined values of the molar absorption coefficients for [Pd(dien)(py)]$^{2+}$, [Pd(dien)(H$_2$O)]$^{2+}$, py, and Hpy$^+$ at 252 nm (2 720, 27, 2 528, and 4 815 cm^2 mmol^{-1}, respectively, and $K_a = 1.99 \times 10^{-6}$ mol dm^{-3} at 25.0 °C, $I = 0.10$) mol dm^{-3}[8] using the Newton System Solver,[9] and a value of $K_{tot.} = 0.124 \pm 0.005$ was obtained.

(b) *Kinetics.* The rate of approach to equilibrium is slow enough for the reaction to be followed spectrophotometrically and the change in the spectrum is consistent with equation (1). The absorbance *vs.* time data were analysed as opposed first- and second-order reactions in the following way.

The absorbance at time *t*, A_t, can be written [equation (3)] in

$$A_t = [I]_t[\varepsilon_1 - \varepsilon_2 - (1 - \alpha_0)\varepsilon_{py} - \alpha_0\varepsilon_{Hpy^+}] \quad (3)$$

terms of the concentration of [Pd(dien)(py)]$^{2+}$ at time, $t = [I]_t$, where ε_1 and ε_2 are the molar absorption coefficients of [Pd(dien)(py)]$^{2+}$ and [Pd(dien)(H$_2$O)]$^{2+}$ at 252 nm and ε_{py} and ε_{Hpy+} are those of py and Hpy$^+$, respectively (the values given above were used); α_0 is the fraction of the released pyridine that is protonated at the acid concentration, $K_a = (1 - \alpha_0)[H^+]/\alpha_0$. The concentration $[I]_t$ is related to time through equation (4),[10] where $[I]_0$ is the known initial con-

$$[I]_t = ([I]_0{}^2 + [I]_0[I]_eE)/([I]_e + [I]_0E) \quad (4)$$

centration of the pyridine complex, $[I]_e$ is its concentration at equilibrium, and E is given by equation (5). Time $t = 0$ was

$$E = \exp\{k_s t([I]_e + [I]_0)/([I]_0 - [I])\} \quad (5)$$

taken as the time of mixing of the reagents and it was assumed that the reaction was sufficiently slow for the errors in assigning time to be negligible. The set of A_t *vs.* time data was fitted by the above equations with $[I]_e$ and k_s (the solvolytic rate constant) as the parameters to be optimized using the Marquardt non-linear optimization algorithm[11] (Figure 2). Within each experiment the values of absorbance A_t calculated from equations (3)—(5) and the optimized values of k_s and $[I]_e$ always agreed with the observed values of A_t to an average standard deviation of less than 0.001 absorbance unit. Residuals were randomly scattered and never greater than 0.002 absorbance unit in absolute value. At convergence, estimated standard errors in the parameters were determined from the corresponding diagonal element of the variance/covariance matrix. Uncertainties quoted are one standard error of estimate. Values of k_s and $[I]_e$ obtained in this way are collected in Table 1 where it will be seen that in all cases studied the protonation of the free

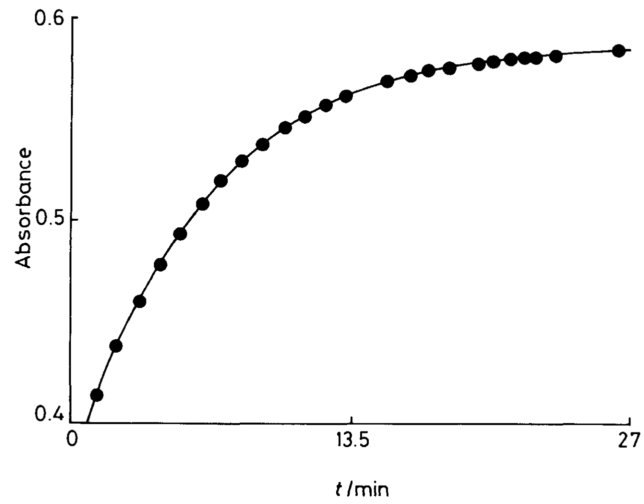


Figure 2. Absorbance *vs.* time data for the approach to equilibrium of equation (1) ([H^+] = 0.2 mol dm^{-3}) at λ = 252 nm

Table 1. Rate and equilibrium constants for the reaction $[Pd(dien)(py)]^{2+} + H_3O^+ \rightleftharpoons [Pd(dien)(H_2O)]^{2+} + Hpy^{+}$ [a]

[H^+]/mol dm^{-3}	$10^3k_5/s^{-1}$	F_{aqua} [b]	$[I]_e$/mol dm^{-3}	$K_{tot.}$
0.0010	3.1 ± 0.1	0.64	3.6×10^{-5}	0.19
0.0050	2.7 ± 0.1	0.87	1.5×10^{-5}	0.14
0.0100	2.7 ± 0.1	0.92	1.0×10^{-5}	0.11
0.0800	2.5 ± 0.1	0.99	1.4×10^{-6}	0.13
0.200	2.5 ± 0.1	1.00	6.0×10^{-7}	0.12
0.400	2.5 ± 0.1	1.00	2.7×10^{-7}	0.13

[a] In aqueous perchloric acid at 25.0 °C, I = 1.00 mol dm^{-3} ($NaClO_4$). [b] Fraction of complex in the form of the aqua species at equilibrium (calculated from $K_{tot.}$). More than 99.5% of the displaced pyridine is protonated for the conditions above (calculated from K_a).

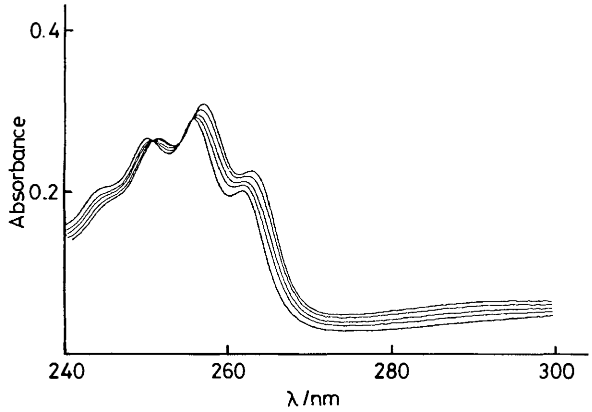


Figure 3. Change in the spectra during the reaction $[Pd(dien)(py)]^{2+} + OH^- \longrightarrow [Pd(dien)(OH)]^+ + py$

pyridine is essentially complete and, for [H^+] > 0.10 mol dm^{-3}, the reaction goes to completion.

(ii) *The Displacement of Pyridine from* $[Pd(dien)(py)]^{2+}$ *in Basic Solution.*—In basic solution, the spectrum of a solution of $[Pd(dien)(py)]^{2+}$ changes to that of an equimolar mixture of $[Pd(dien)(OH)]^+$ and py with three well defined isosbestic points, Figure 3. When a sufficient excess of NaOH is present there is no interference from the hydroxo-bridged dimer or any other polymeric species and the spectrophotometric change is first order. The rate constants, obtained by fitting the absorbance, A_t *vs.* time (t) data to the expression $A_t = A_\infty - (A_\infty - A_0)\exp(-k_{obs.}t)$, with A_0, A_∞, and $k_{obs.}$ as variable parameters to be optimized, are collected in Table 2. The rate equation takes the form $10^3k_{obs.} = (2.33 \pm 0.1) + (6.3 \pm 0.8)[OH^-] + (8.05 \pm 0.9)[OH^-]^2$ s^{-1} (uncertainties are one standard error of estimate determined from polynomial regression).

Table 2. First-order rate constants for the reaction $[Pd(dien)(py)]^{2+} + OH^- \longrightarrow [Pd(dien)(OH)]^+ + py$ [a]

[OH^-]/mol dm^{-3}	$10^3k_{obs.}/s^{-1}$	$10^3k_{calc.}$ [b]$/s^{-1}$
0.0500	2.70 ± 0.1	2.67
0.100	3.32 ± 0.1	3.04
0.200	3.95 ± 0.2	3.91
0.300	5.02 ± 0.1	4.95
0.400	6.22 ± 0.1	6.14
0.500	7.57 ± 0.2	7.50

[a] In water at 25.0 °C, I = 1.0 mol dm^{-3} ($NaClO_4$). [b] Calculated using the expression $10^3k_{obs.} = 2.33 + 6.3[OH^-] + 8.05[OH^-]^2$ s^{-1}.

(iii) *The Reversible Reaction of* $[Pd(dien)(py)]^{2+}$ *with Chloride in Aqueous Solution.*—(a) *Equilibria.* When solid sodium chloride (150 mg) is dissolved in a solution of $[Pd(dien)(py)][ClO_4]_2$ (3.91 mg) in D_2O (5.0 cm^3), [complex] = 1.6×10^{-2} and [Cl^-] = 5.0 mol dm^{-3}, the 400-MHz ^1H n.m.r. spectrum changes significantly, Figure 1. The doublet assigned to the H^2 and $H^{2'}$ protons is shifted from δ 8.60 to 8.73 and somewhat broadened, while the triplets assigned to H^3 and $H^{3'}$ and the multiplet assigned to H^4 are also broadened and shifted by δ 0.06. The signals from the protons of dien are also broadened and shifted by δ 0.06. Small unresolved humps are seen where free pyridine resonates and broad signals in the CH_2 region could be due to the presence of small amounts of the chloro complex. Addition of a three-fold molar excess (*ca.* 5×10^{-2} mol dm^{-3}) of pyridine does not affect the chemical shifts of this spectrum but introduces new peaks, assigned to free pyridine at δ 7.50, 7.92, and 8.56, with much the same coupling as for the co-ordinated pyridine. The spectrum is sharpened and the broad signals, tentatively assigned to the chloro complex, disappear, Figure 1. It must therefore be concluded that the addition of chloride ions leads to the conversion of most of the substrate into a new species in which the pyridine is still bound to palladium, together with a small amount of the chloro complex and free pyridine. The rate of exchange of free and co-ordinated pyridine is reasonably fast but not fast enough to lead to coalescence of signal. Addition of a small molar excess of pyridine does not convert the material back into the original substrate but does remove the chloro species and slows down the exchange between free and co-ordinated pyridine. It is therefore concluded that the exchange of pyridine takes place through the four-co-ordinate chloro complex and that direct exchange between free and co-ordinated pyridine in the adduct is very slow indeed. In this adduct the dien is either symmetrically bound as a terdentate or else acts as a bidentate ligand in which the free ends exchange very rapidly. However, the chemical shifts of the dien protons are not changed sufficiently, nor are they changed selectively when the adduct is formed and displacement of a terminal NH_2 must be ruled out. It must therefore be concluded that the intermediate is a five-co-ordinate species although a loose binding of the central nitrogen cannot be ruled out completely.

In more dilute aqueous solution ([complex] = 10^{-4} mol dm^{-3}) the addition of NaCl has a considerable effect upon the u.v. spectrum (Figure 4). At first sight the change in spectrum

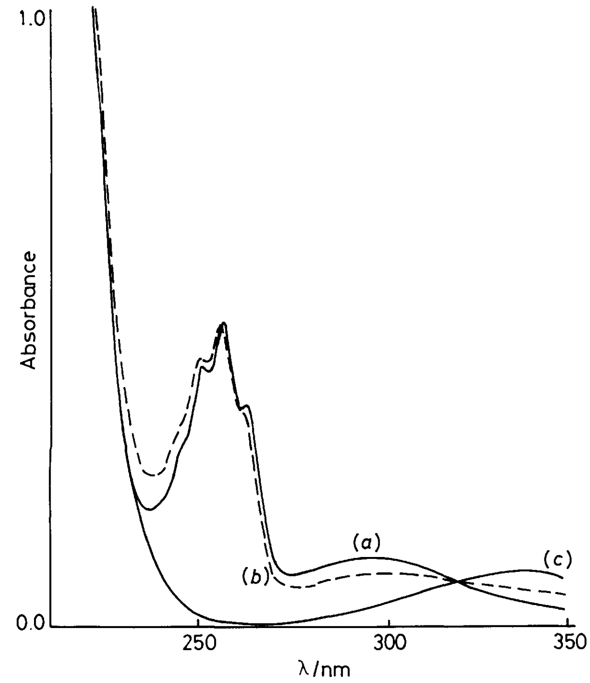


Figure 4. Change in the spectrum of an aqueous solution of $[Pd(dien)(py)][ClO_4]_2$ (1.33×10^{-4} mol dm^{-3}) (*a*) on the addition of NaCl (0.050 mol dm^{-3}) (*b*). Also shown is the spectrum of an authentic sample of $[Pd(dien)Cl]Cl$ (1.33×10^{-4} mol dm^{-3}) (*c*)

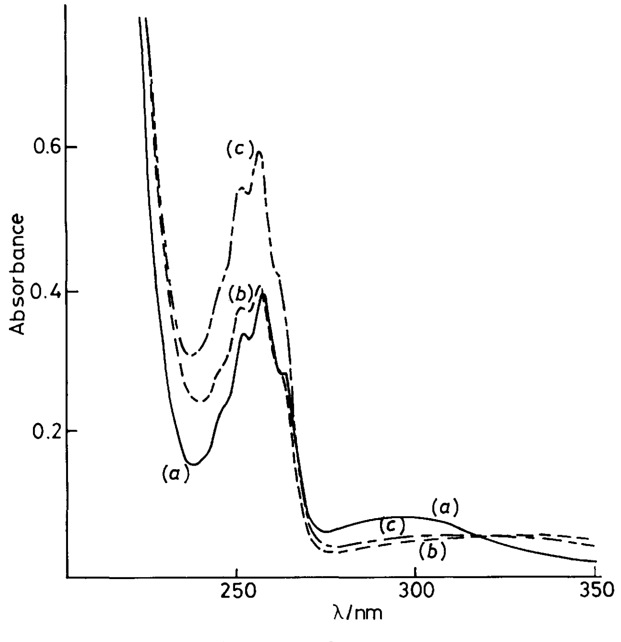


Figure 5. The effect of adding excess of pyridine to an aqueous solution of $[Pd(dien)(py)][ClO_4]_2$ (1.33×10^{-4} mol dm^{-3}) and excess of NaCl. (*a*) Complex alone, (*b*) solution (*a*) + excess of NaCl, and (*c*) solution (*b*) + excess of pyridine

Table 3. Specific first-order rate constants for approach to equilibrium in the reaction $[Pd(dien)(py)]^{2+} + Cl^- \rightleftharpoons [Pd(dien)(py)Cl]^+$ *

$[Cl^-]$/mol dm^{-3}	$10^2\ k_{obs.}$/s^{-1}
0.100	3.7 ± 0.1
0.150	4.3 ± 0.2
0.200	4.6 ± 0.2
0.300	5.7 ± 0.2
0.400	6.2 ± 0.1
0.500	7.6 ± 0.1

* In water at 25.0 °C, I = 1.0 mol dm^{-3} ($NaClO_4$).

between 270 and 350 nm appears to indicate a simple reversible displacement reaction of the type (6), since the intermediate

$$[Pd(dien)(py)]^{2+} + Cl^- \overset{K_{Cl}}{\rightleftharpoons} [Pd(dien)Cl]^+ + py \quad (6)$$

spectra appear to pass through the crossing point of the spectra of authentic samples of the pyridine and the chloro species. However, the change in the spectra in the region where free pyridine absorbs is not consistent with the release of pyridine, *cf.* Figure 3 where the spectral changes due to the replacement of py by OH^- can be clearly seen. Addition of free pyridine does not greatly change the spectrum in the region where pyridine is transparent (Figure 5).

Analysis of the dependence of the absorbance of an equilibrated solution at 296 nm as a function of $[Cl^-]$ shows that the substrate is distributed between more than two absorbing species and large systematic errors could not be eliminated when attempts were made to fit the absorbance (A) *vs.* $[Cl^-]$ data to an expression of the type (7) where $\varepsilon_{M(py)}$ and

$$A = \varepsilon_{M(py)}c_0 + \tfrac{1}{2}(\varepsilon_{M(py)} - \varepsilon_{MCl})\{(K_{Cl}^2[Cl^-]^2 + 4K_{Cl}[Cl^-]c_0)^{\frac{1}{2}} - K_{Cl}[Cl^-]\} \quad (7)$$

ε_{MCl} are the known molar absorption coefficients of $[Pd(dien)(py)]^{2+}$ and $[Pd(dien)Cl]^+$, c_0 is the known concentration of the complex, and K_{Cl} is the value of the equilibrium constant for equation (6) to be optimized.

By introducing an intermediate species, (I), containing both pyridine and chloride [equation (8)], the dependence of

$$[Pd(dien)(py)]^{2+} + Cl^- \overset{K_1}{\rightleftharpoons} (I) \overset{K_2}{\rightleftharpoons} [Pd(dien)Cl]^+ + py \quad (8)$$

absorbance upon $[Cl^-]$ takes the form (9) where x is defined as

$$A = \varepsilon_{M(py)}(c_0 - x^2/K_2 - x) + \varepsilon_I x^2/K_2 + \varepsilon_{MCl}x \quad (9)$$

in equation (10). The absorbance of pyridine at this wavelength

$$x = \{[K_1^2K_2^2[Cl^-]^2 + 4K_1K_2[Cl^-]c_0(1 + K_1[Cl^-])]^{\frac{1}{2}} - K_1K_2[Cl^-]\}/2(1 + K_1[Cl^-]) \quad (10)$$

is negligible. Using independently determined values for $c_0 = 4.76 \times 10^{-4}$ mol dm^{-3}, $\varepsilon_{M(py)}$ and ε_{MCl} = 592 and 155 cm^2 mmol^{-1}, respectively at 296 nm, curve fitting with three parameters gives optimum values of $K_1 = 4.58 \pm 0.47$ dm^3 mol^{-1}, $K_2 = (3.58 \pm 2.32) \times 10^{-6}$ mol dm^{-3}, and $\varepsilon_I = 368 \pm 4$ cm^2 mmol^{-1}, (uncertainties are one standard error of estimate). The error in K_2 is large because, even at the highest concentrations of chloride used (0.5 mol dm^{-3}), only about 8% of the substrate is in the form of the chloro complex.

(b) *Kinetics.* The system does not reach equilibrium instantaneously and it is possible to follow the change by normal u.v. spectrophotometry. The half-lives are too short to allow a precise evaluation of the kinetics but in the range of added chloride, $0.10 < [Cl^-] < 0.50$ mol dm^{-3}, the approach to equilibrium follows a first-order rate law and the rate constants, $k_{obs.}$, vary with $[Cl^-]$, Table 3. Plots of $k_{obs.}$ *vs.* $[Cl^-]$ are linear, with $k_{obs.} = k_a + k_2[Cl^-]$, where $k_a = (2.75 \pm 0.20) \times 10^{-2}$ s^{-1} and $k_2 = (9.3 \pm 0.7) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}.

Discussion

The $[Pd(dien)(py)]^{2+}$ cation is stable in aqueous solution and requires the addition of acid to push the equilibrium towards the aqua species. The best fit of the absorbance *vs.* $[H^+]$ data at equilibrium gives the value of $K_{tot.} = 0.124 \pm 0.005$ for equilibrium (1). Combined with the equilibrium constant for the deprotonation of the pyridinium cation, $K_a = 1.99 \times 10^{-6}$ mol dm^{-3}, equilibrium (2), this gives a value for the instability constant of the pyridine complex, $K_s = (2.48 \pm 0.10) \times 10^{-7}$ mol dm^{-3} [equilibrium (11)].

$$[Pd(dien)(py)]^{2+} + H_2O \overset{K_s}{\rightleftharpoons} [Pd(dien)(H_2O)]^{2+} + py \quad (11)$$

The rate at which the system approaches equilibrium is slow enough to be followed kinetically and the analysis of the absorbance *vs.* time data in terms of reversible first- and second-order processes gives a value for k_s, the solvolytic rate constant, of 2.5×10^{-3} s^{-1}. The data in Table 1 suggest a small increase in the value as the position of equilibrium moves away from the aqua complex and the possibility of a small amount of interference from the acid dissociation and/or the dimerization of the aqua complex has been considered. Analysis of the pH *vs.* NaOH titre curve for a fresh solution of the aqua complex is only possible if the dimerization equilibrium (12) with $K_d = 3.1 \times 10^{-6}$ is also taken into account. This value and the

$$2[Pd(dien)(H_2O)]^{2+} \overset{K_d}{\rightleftharpoons} [(dien)Pd(OH)Pd(dien)]^{3+} + H_3O^+ \quad (12)$$

resulting pK_a of the aqua complex, 7.36, are in good agreement with those in the literature measured under similar conditions[12,13] and it can be easily calculated that, even at the lowest acid concentration used, the concentration of the hydroxo species and the dimer would be negligible. Therefore, the deviations cannot be accounted for in this way. The analysis of the kinetics in terms of reversible first- and second-order reactions gives optimized values for $[I]_e$, the concentration of the pyridine complex at equilibrium and these can be used to obtain values for $K_{tot.}$, provided the position of the equilibrium is sufficiently far from complete reaction. These values are also included in Table 1 and compare favourably with those determined from the dependence upon $[H^+]$ of the absorbance of the solution at the end of the reaction.

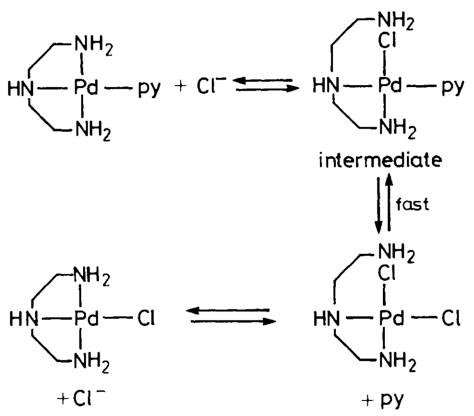
Combination of k_s with K_s gives an estimate of the rate constant for the displacement of water by pyridine, $k_{py} = k_s/K_s = 1.0 \times 10^4$ dm^3 mol^{-1} s^{-1}. This is nearly four orders of magnitude greater than the rate constant for chloride anation (3.8 dm^3 mol^{-1} s^{-1})[14] and contrasts with the observation that, in the reactions of the sterically hindered Et$_4$dien [Et$_4$dien = 1,5-bis(diethylamino)-3-azapentane] complex, pyridine is less reactive than chloride towards the aqua complex. The direct determination of the rate constants for the displacement of H_2O from $[Pd(dien)(H_2O)]^{2+}$ has yet to be made but such a large difference in reactivity between chloride and pyridine in replacing water or methanol from platinum(II) is well known, not only with the pyridine 10^3 times more reactive than Cl^- [15–17] but also the other way round.[18]

The displacement of pyridine from $[Pd(dien)(py)]^{2+}$ in basic solution takes place in a single stage and, because of the high stability of the hydroxo complex, goes to completion. There is no complication from dimer formation. However, the rate equation takes the form $k_{obs.} = k_s + k_1[OH^-] + k_2[OH^-]^2$. The $[OH^-]$-independent term (2.33×10^{-3} s^{-1}) is sufficiently close in value to k_s determined in acid solution (2.45×10^{-3} s^{-1}) for it to be identified as the rate constant for the solvolytic displacement of pyridine. The appearance of first- and second-order dependences on $[OH^-]$ is becoming quite common in the base hydrolysis of some dicationic complexes of platinum(II), *e.g.*, $[PtL_2(Me_2S)_2]^{2+}$ (L = NH$_3$,[19] or Me$_2$S[20]), but is absent in the reactions of $[Pd(NH_3)_4]^{2+}$,[20] where the loss of the first ammonia takes place at a rate that is the same in acidic, neutral, and basic solution. On rare occasions, the behaviour is also found with monocationic species, *e.g.* $[Pt(dien)(RCO_2)]^+$ (R = CCl$_3$, CHCl$_2$, or CH$_2$Cl)[21] and marginally with $[Pd(dien)Br]^+$.[22] It is not yet clear whether this type of behaviour is due to a single mechanistic feature and, while we are of the opinion that it arises, in part at least, from ion association between the cation and hydroxide, we are unable to account for its participation in the reaction of $[Pd(dien)(py)]^{2+}$ while being absent from that of $[Pd(NH_3)_4]^{2+}$.

The main reaction between $[Pd(dien)(py)]^{2+}$ and NaCl does not appear to be the simple ligand-displacement equilibrium shown in equation (6) which can be seen separately and suppressed by the addition of small amounts of pyridine. The effect of added chloride on the ^{1}H n.m.r. spectrum is not consistent with the release of pyridine, and the changes of the u.v. spectrum in regions where pyridine does not absorb are consistent with the formation of a species in which both chloride and pyridine are co-ordinated to the palladium. The equilibrium constant for adduct formation, $K_1 = (4.58 \pm 0.50)$ dm^3 mol^{-1}, and that for its dissociation to product, $K_2 = (3.6 \pm 2.0) \times 10^{-6}$ mol dm^{-3}, can be combined to give the ligand-displacement equilibrium constant for equation (6), $K_{Cl} = K_1K_2 = (1.5 \pm 0.9) \times 10^{-5}$. The rate constant for the faster process, measured under pseudo-first-order conditions, follows the rate equation $10^2k_{obs.} = (2.75 \pm 0.2) + (9.3 \pm 0.7)[Cl^-]$ s^{-1}. This is further support for the conclusion that the process is not the single displacement of pyridine because the chloride-independent term is about ten times greater than the solvolytic rate constant observed in both acidic and basic solution in the absence of chloride. We propose that the rate law does indeed belong to the opposed reactions corresponding to the first part of reaction (8), the chloride-independent term, k_a, being the sum of the rate constants for solvolysis of the substrate (2.5×10^{-3} s^{-1}) and that for the dissociation of the intermediate back to reagents, k_{-1}. The ratio of the rate constants, $k_{Cl}/k_{-1} = 9.3$ dm^3 mol^{-1} s^{-1}/[(2.75 − 0.25) × 10^{-2} s^{-1}] = 3.7 dm^3 mol^{-1}, is, within the limit of experimental errors, equal to the directly determined equilibrium constant, K_1 (4.6 dm^3 mol^{-1}).

Breet and Van Eldik,[23] looking at the reactions between $[Pd(dien)Cl]^+$ and nucleosides and similar species, observed departures from the simple behaviour expected for usual type of associative substitution and ascribed it to ion-association interaction between the reagents. However, the possibility that the equilibrium constant, K_1, relates to simple ion association between the dication and chloride is extremely unlikely as such processes are diffusion controlled whereas this system reacts slowly enough to be followed by classical spectrophotometric techniques. Five-co-ordination, in which the amine ligand remains in the plane and the chloride takes up an axial site, is not so far removed from ion association that its rate is likely to be significantly slower. The involvement of a more disturbed five-co-ordination is called for but this is usually accompanied by dramatic spectral changes which are not observed in this system.

Many years ago Coe and Lyons[6] examined the reactions of $[Pd(dien)(NH_3)]^{2+}$ in acidic solution in the presence and absence of chloride. Direct comparison can be made with the reactions of $[Pd(dien)(am)]^{2+}$ (am = amine) with acid alone. These are simple first-order processes that are irreversible when sufficient acid is present. The change of am from NH$_3$ to pyridine increases the rate constant, as might be expected from the decrease in the basicity of the leaving group, but by an amount that is less than might be predicted from the difference



in basicity (6.0×10^{-4} to 2.4×10^{-3} s^{-1}). Coe and Lyons reported anomalous behaviour in the displacement of ammonia by Cl^- in the presence of acid. Two exponential changes were observed and the kinetic analysis supported two parallel processes, the faster of which was the opening of a chelate ring and the slower the displacement of pyridine. The complex was prepared *in situ* in the presence of excess of ammonia and the displacement of ammonia could only be studied in the presence of excess of acid. Stabilization of ring opening in polyamine chelate complexes in acidic solution is well established but usually, and especially in the absence of strongly competing ligands, the ring will close again rapidly when the acid concentration is reduced.[24–26]

However, until the $[Pd(dien)(NH_3)]^{2+}$ cation is isolated as a crystalline salt, a study of its reaction with chloride in the absence of acid cannot be carried out. We are in the process of extending our study to complexes of the type $[Pd(dien)(am)]^{2+}$ where am is an amine or an heterocyclic nitrogen base but, until now, we have been unable to isolate the ammonia complex.

The reactions of $[Pd(dien)(py)]^{2+}$ with Cl^- have also been studied in the presence of acid but we do not observe the biphasic kinetics reported for the ammonia analogue. The reaction proceeds in a single first-order stage (although the statistics of the curve fitting suggest the possibility of slight inconsistencies which are not beyond the possibility of experimental error) and the rate constants depend upon $[Cl^-]$ and decrease as $[H^+]$ is increased. The analysis of data and the interpretation are complicated by the observed instability of the expected product, $[Pd(dien)Cl]^+$ which, in the presence of both H^+ and Cl^-, undergoes further reaction, presumably ring opening, and discussion of the reaction of the pyridine complex in the presence of both acid and chloride must be deferred until this aspect has been fully investigated.

In view of the work of Coe and Lyons, the possibility that the intermediate containing both pyridine and chloride is nothing more complicated than a four-co-ordinate species in which dien is acting as a bidentate ligand must be considered.

The constants of equilibria of the type, $[PdL'(am)]^{2+} + Cl^- \rightleftharpoons [PdL'Cl]^+ +$ am, where L′ is a tridentate linear amine will be expected to depend upon the basicity of am, the greater the basicity the smaller the equilibrium constant. The binding of a primary amine (pK_a of $Ham^+ > 10$) would be much stronger than that of pyridine ($pK_a = 5.9$). In addition, the chelate effect would make a substantial reduction in the equilibrium constant if the primary amine were part of a chelate system. In acidic solution, protonation of the NH_2 group might stabilize the ring-opened form but it would also prevent the reattachment of pyridine (or ammonia). We therefore conclude that ring opening is not the correct explanation of this phenomenon. The ^1H n.m.r. spectra of $[Pd(dien)(py)]^{2+}$ in the presence or absence of Cl^- give no indication of unsymmetrical binding of dien. This cannot be explained in terms of a dynamic system because the rate constant for the change after chloride is added is far too small.

We therefore conclude that the intermediate is indeed five-co-ordinated, but, at this stage, we take the view that until we have mapped the extent of this phenomenon and have established the important parameters it would be futile to speculate further.

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