Inorganica Chimica Acta, *188* (1991) 25–32

Effect of steric hindrance on kinetic and equilibrium data for substitution reactions of diaqua(N-substituted ethylenediamine)palladium(II) with chloride in aqueous solution

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(Received February 28, 1991; revised May 21, 1991)

Abstract

Kinetic and thermodynamic data are reported for the complex formation reactions: $Pd(R_4en)(H_2O)_2^{2+}Cl^- \overset{K_1}{\rightleftharpoons} Pd(R_4en)(H_2O)Cl^+ + H_2O$ and $Pd(R_4en)(H_2O)Cl^+ + Cl^- \overset{K_2}{\rightleftharpoons} Pd(R_4en)Cl_2 + H_2O$, as a function of steric hindrance for R = Me and Et. The reported rate constants for these reactions decrease drastically on increasing the steric hindrance. These findings along with strongly negative $\Delta S^{\neq}$ values support the operation of an associative reaction mechanism. Values for the complex formation and acid-dissociation constants are reported, from which speciation plots are constructed. All the results are discussed in reference to the corresponding data for the unsubstituted en system and the *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ species.

Introduction

Substitution reactions of square planar complexes of d^8 metal ions, such as Pt(II) and Pd(II), generally follow an associative substitution mechanism with the characteristic two-term rate law $k_{obs} = k_a + k_b[Y]$, where Y is the entering nucleophile. This rate law can be interpreted in terms of either two parallel reactions in which the k_a path represents a solvolysis reaction step that is followed by a rapid reaction with Y, or a reversible substitution process in which the k_a path represents the contribution from the reverse reaction step, i.e. for instance solvolysis of the substitution product. Earlier studies from our laboratories [1–5] have clearly demonstrated that steric hindrance on the non-participating ligands cannot affect the nature of the substitution mechanism, although it can slow down the reaction by many orders of magnitude. A changeover in mechanism from associative to dissociative is only observed when strong *trans*-labilizing ligands are introduced in the coordination sphere [6].

In a recent study [7] we investigated the subtitution reactions of $Pd(en)(H_2O)_2^{2+}$ (en = ethylenediamine), firstly as an extension of our earlier work on the diethylenetriamine (dien) and substituted dien complexes [1–5], and secondly in an effort to come closer to the substitution behaviour of the corresponding *cis* − $Pt(NH_3)_2(H_2O)_2^{2+}$ species that exhibits important biological properties in terms of its antitumor activity [8]. The introduction of steric hindrance on the en ligand can be used to tune the lability of this metal center and so control its reactivity in possible catalytic and biological applications. For this reason we have performed a systematic study of the substitution reactions of $Pd(R_4en)(H_2O)_2^{2+}$ with chloride in acidic aqueous solution, in which R_4 en represents N-substituted ethylenediamine and R = Me, Et. The kinetic and thermodynamic data reported in this study are compared with those reported for the unsubstituted complex, i.e. R = H [7].

Experimental

Materials

The $Pd(R_4en)Cl_2$ complexes were prepared according to the procedure published for $Pd(en)Cl_2$ [7]. For R = Me and Et, *N,N,N′,N′*-tetramethylethylenediamine ($C_6H_{16}N_2$) and *N,N,N′,N′*-tetraethylethylenediamine ($C_{10}H_{24}N_2$), respectively, were used instead of the unsubstituted en ligand. The experimental analyses [9] were in good agreement

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0020-1693/91/$3.50

with the theoretically expected values. Calc. for $Pd(Me_4en)Cl_2$: C, 24.5; H, 5.49; N, 9.54; %Cl, 24.2. Found: C, 24.8; H, 5.47; N, 9.72; Cl, 24.2%. Calc. for $Pd(Et_4en)Cl_2$: C, 34.3; H, 6.92; N, 8.01; Cl, 20.3. Found: C, 34.4; H, 6.76; N, 8.06, Cl, 20.4%. IR and UV–Vis spectra were in excellent agreement with the available literature data [10, 11]. Stock solutions of the diaqua complexes were prepared by treating the chloro complexes with at least two equivalents of dried $AgClO_4$, followed by precipitation of AgCl. Any excess of Ag^+ ions in solution was removed by adjusting the pH to 12–13, followed by the precipitation and filtration of Ag_2O. All reactions were carried out using chemicals of analytical reagent grade and deionized water. $NaClO_4$ was used to adjust the ionic strength of the test solutions to 0.10 M. $HClO_4$ and NaOH were employed to adjust the pH of the test solutions.

Instrumentation

UV–Vis absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer equipped with a thermostated (± 0.1 °C) sample cell holder. IR spectra were recorded on a Nicolet 5-SX instrument. Kinetic measurements were performed on a Durrum D110 stopped-flow instrument coupled to an on-line data acquisition system [12]. The investigated reactions exhibited good first-order behaviour for up to three half-lives of the reaction under pseudo-first-order conditions, i.e. at least a ten-fold excess of one of the reaction partners. Equilibrium constants were also measured potentiometrically with the aid of an ion-selective electrode (ISE) for Cl^-. For this purpose a WTW microprocessor ion meter, an Ingold ISE ($AgCl/Ag_2S$) and a reference system (AgCl/Ag) including a NH_4NO_3 salt bridge were used [7]. This system was calibrated daily by constructing a plot of electrode potential (mV) versus $\log[Cl^-]$ for the range $10^{-4} \leqslant [Cl^-] \leqslant 10^{-2}$ M. The slope of the linear correlation varied between 56 and 59 mV with an average value of 57 mV, which is close to the theoretically expected value, viz. 59 mV, under these conditions. The same system was used to measure the pH of the test solution by replacing the Cl^- electrode with a conventional glass electrode. The purpose of NH_4NO_3 in the salt bridge instead of the usually employed KNO_3 was to prevent the possible precipitation of $KClO_4$, since the test solutions contained relatively high ClO_4^- concentrations. The bridge electrolyte was replaced daily to prevent any serious contamination.

Results and discussion

Based on our experience with the kinetic and thermodynamic behaviour of the $Pd(en)(H_2O)_2^{2+}-Cl^-$ system [7], the experimental conditions for the present investigation were selected in such a way that the composition of the test solutions could be well defined. In addition, extrapolation to biologically relevant conditions (for instance a particular $[Cl^-]$ and pH) in terms of the model character of the selected complexes, is possible on the basis of the reported kinetic and thermodynamic data.

Equilibrium studies

The complex formation equilibria of $Pd(R_4en)(H_2O)_2^{2+}$ with Cl^- were investigated at a pH of *c.* 3 in order to prevent the participation of hydroxo species. Complex formation is accompanied by significant spectral changes in the range 350–400 nm as illustrated by the typical examples given in Fig. 1 for the overall reactions in (1). These spectral changes are very typical for this type of complexes (see Figs. 1 and 2 in ref. 7) and in general indicate a shift to longer wavelength on the formation of the dichloro complex. On dissolution of the isolated dichloro complex (Fig. 1(b)), spontaneous solvolysis produces a mixture of all three complex species via the reverse reactions in (1). The dichloro complex can be stabilized in the presence of an excess of

$$Pd(R_4en)(H_2O)_2^{2+} + Cl^- \overset{K_1}{\rightleftharpoons} Pd(R_4en)(H_2O)Cl^+ + H_2O \tag{1}$$

$$Pd(R_4en)(H_2O)Cl^+ + Cl^- \overset{K_2}{\rightleftharpoons} Pd(R_4en)Cl_2 + H_2O$$

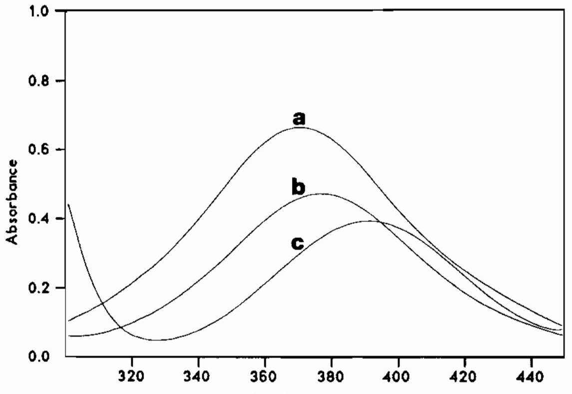

Fig. 1. UV–Vis spectra of $Pd(Et_4en)$ complexes in aqueous solution. Experimental conditions: $[Pd(II)] = 1.0 \times 10^{-3}$ M; optical pathlength = 1.0 cm; pH ≈ 3. (a) Solution of $Pd(Et_4en)(H_2O)_2^{2+}$, $\lambda_{max} = 365$–370 nm. (b) Equilibrated solution of $Pd(Et_4en)Cl_2$ dissolved in water, $\lambda_{max} = 375$ nm. (c) After addition of large excess of solid NaCl to solution b, $\lambda_{max} = 392$ nm.

Cl^- (Fig. 1(c)), although this can lead to the precipitation of the dichloro complex in the case of the less soluble Et_4en complex. The observed spectral properties (given as $\lambda_{max}(\epsilon)$) for $Pd(R_4en)(H_2O)_2^{2+}$ are 340–343(270), 363–365(600) and 366–371 nm (620 M^{-1} cm^{-1}) for R = H, Me and Et, respectively, and for $Pd(R_4en)Cl_2$ are 371(360), 385(450) and 392 nm (475 M^{-1} cm^{-1}) for R = H, Me and Et, respectively.

The complex formation constants K_1 and K_2 were determined using the ion-selective Cl^- electrode mentioned above. This was done by titrating known quantities of $Pd(R_4en)(H_2O)_2^{2+}$ with a standardized Cl^- solution, and measuring the free $[Cl^-]$ after equilibrium has been established. The relative amounts of added Cl^- determined whether K_1 or K_2 could be estimated. Details of this procedure are reported elsewhere [7]. The formation constants were found to have the values $K_1 = 4000 \pm 160$, 3200 ± 500 and 2820 ± 170 M^{-1}, and $K_2 = 130 \pm 14$, 105 ± 14 and 52 ± 9 M^{-1} for R = H, Me and Et, respectively, at 25 °C, pH ≈ 3 and 0.10 M ionic strength. Both K_1 and K_2 decrease on increasing steric hindrance on the en ligand, which requires that a larger excess of Cl^- is needed to produce the dichloro complex quantitatively. The values of K_1 and K_2 for the Et_4en complexes are such that an increasing concentration of the chloroaqua complex may exist in solution compared to the other diamine ligands employed. Thus increasing steric hindrance may lead to the stabilization of a particular hydrolysis product.

In addition to the equilibria given in (1), the aqua complexes exhibit characteristic acid–base equilibria as indicated in (2). All the diaqua complexes exhibit only one inflection during the titration with base,

$$Pd(R_4en)(H_2O)_2^{2+} \overset{K_3}{\rightleftharpoons} Pd(R_4en)(H_2O)OH^+ + H^+ \qquad (2)$$

$$Pd(R_4en)(H_2O)Cl^+ \overset{K_4}{\rightleftharpoons} Pd(R_4en)(OH)Cl + H^+$$

exactly at the point where an equimolar concentration of base had been added. A typical example of such a titration curve is presented in Fig. 2. The absence of a second deprotonation step in such titrations is ascribed to the quantitative formation of a dihydroxo-bridged dimeric species as shown in (3) [7, 13]. The deprotonation of the chloroaqua complexes can

$$2Pd(R_4en)(H_2O)OH^+ \rightleftharpoons (R_4en)Pd(\mu\text{-}OH)_2Pd(R_4en)^{2+} \qquad (3)$$

only be studied in an indirect way since these species are always in equilibrium with the corresponding diaqua and dichloro complexes. By titrating the dichloro complex with base in the presence of a large excess of Cl^- (to ensure the formation of the dichloro complex), deprotonation of the chloroaqua complex (always present at low concentrations as a result of spontaneous solvolysis [1, 7]) will produce the substitution inert chlorohydroxo species and so prevent the formation of the dichloro complex. Thus there will be a build-up of $Pd(R_4en)(OH)Cl$ during the titration that will correspond to the pK_4 value of the chloroaqua complex. The acid dissociation constants were found to have the values $pK_3 = 5.6 \pm 0.2$, 5.4 ± 0.2 and 5.8 ± 0.2, and $pK_4 = 7.3 \pm 0.2$, 7.0 ± 0.2 and 7.7 ± 0.2 for R = H, Me and Et, respectively, at 25 °C and 0.1 M ionic strength. These data exhibit a general decrease in pK_3 and

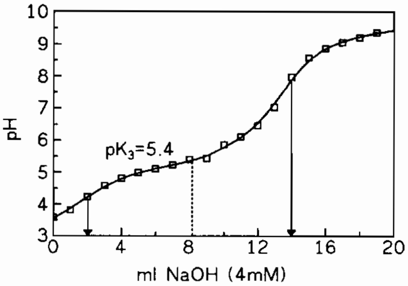

Fig. 2. pH titration of $Pd(Me_4en)(H_2O)_2^{2+}$. Experimental conditions: $[Pd(II)] = 2.4 \times 10^{-3}$ M; ionic strength = 0.10 M; volume of solution = 20 ml; stock solution of diaqua complex was slightly acidified (see 'Experimental').

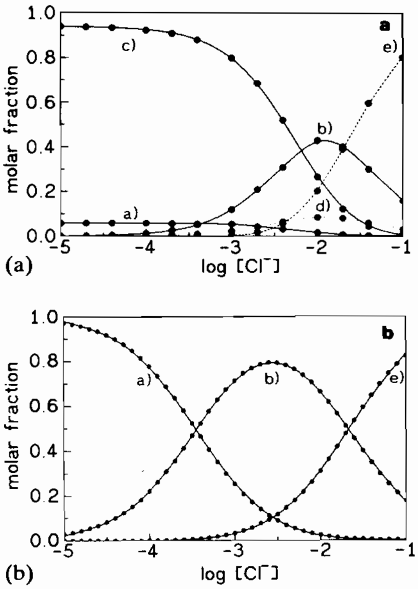

Fig. 3. Distribution curves for $Pd(Et_4en)$ complexes as a function of $[Cl^-]$ and pH at 25 °C and 0.10 M ionic strength. (a) pH = 7: a, $Pd(Et_4en)(H_2O)_2^{2+}$; b, $Pd(Et_4en)(H_2O)Cl^+$; c, $Pd(Et_4en)(H_2O)OH^+$; d, $Pd(Et_4en)(Cl)OH$; e, $Pd(Et_4en)Cl_2$. (b) pH = 3: a, b and e as for Fig. 3(a). Data points are calculated values.

pK_4 on going from the unsubstituted to the Me$_4$en complexes, followed by an increase in these values on going to the Et$_4$en complexes. Inductive effects of the methyl substituents presumably cause an increase in the acidity of coordinated water, whereas steric effects in the case of the ethyl substituents can account for the less labile coordinated water molecules and a decrease in acidity [1–6]. Such effects should also clearly show up in the kinetics of the substitution processes (see further 'Discussion').

The reported values of K_1, K_2, K_3 and K_4 enable us to estimate the concentration of all complexes present in solution as a function of pH and [Cl$^-$]. For the calculation of the distribution of species in solution, an iterative procedure based on the Newton–Raphson method for solving simultaneous equations, was used, for which the algorithms are described elsewhere [14–16]. Two typical examples of such distribution curves are given in Fig. 3 for pH = 3 and 7, respectively. A comparison of the two examples clearly demonstrates the importance of hydroxo species at pH 7, i.e. close to physiological conditions, which are only present at very low levels at pH 3. A comparison of these plots with that reported before for the unsubstituted en system [7], clearly demonstrates the larger fraction of chloroaqua species produced in the case of the Et$_4$en system as predicted above. Such distribution curves also demonstrate the important influence of the free [Cl$^-$], especially in terms of the large variation in [Cl$^-$] under physiological conditions.

Kinetic studies

The complex formation reactions of Pd(R$_4$en)(H$_2$O)$_2$$^{2+}$ can be followed conveniently on a stopped-flow instrument at a wavelength where the maximum absorbance change occurs according to the spectral data reported above. On treating the diaqua complex with chloride, two subsequent kinetic steps are observed in the absorbance–time traces. The rate constants of the steps are such that they can be easily separated and both steps exhibit a dependence on the [Cl$^-$]. These findings can be best interpreted in terms of the two complex formation reactions given in (1), for which the forward and reverse reactions have the rate constants k_1, k_{-1}, k_2 and k_{-2}, respectively. A summary of the observed rate constants for the different complex formation reactions is given in Table 1. The observed rate constants exhibit a chloride concentration dependence, $k_{obs} = k_a + k_b$ [Cl$^-$] (Fig. 4), that is typical for substitution reactions of square planar complexes (see 'Introduction'), and the values of k_a and k_b are included in Table 1. Some experiments on the en system [7] were repeated at different temperatures in order to also be able to estimate the activation parameters for this system. In some cases the temperature range for these measurements was restricted by the high reactivity of the species. The pressure dependence of these reactions was not studied, partly due to the extreme reactivity of some of the complex species.

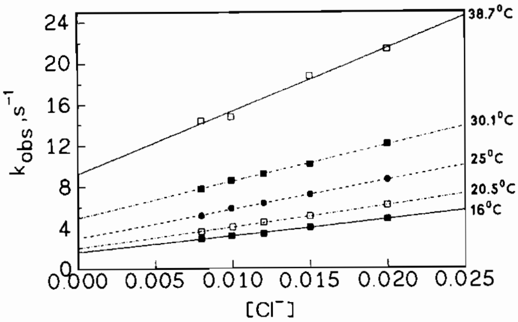

Fig. 4. Typical plots of k_{obs} vs. [Cl$^-$] for the reaction of Pd(Me$_4$en)(H$_2$O)Cl$^+$ with Cl$^-$ as a function of temperature (data taken from Table 1).

The results in Table 1 clearly demonstrate that $k_a \approx 0$ within the experimental error limits for the first complex formation step, i.e. $k_{-1} \approx 0$. The values of k_b for the first step represent those for k_1. No parallel solvolysis reaction can exist for the anation of the diaqua complexes, such that k_a must be related to the reverse reaction step (k_{-1}), which is very small due to the rather high values of $K_1 (= k_1/k_{-1})$. The second complex formation step exhibits meaningful values for k_a and k_b, where the latter can be assigned to k_2. In this case k_a can either represent a parallel solvolysis reaction (k_{-1}), or the solvolysis reaction of the dichloro reaction product (k_{-2}), or a combination of both steps [7]. In order to resolve these possibilities, k_{-2} was measured in a direct way via the base hydrolysis of Pd(R$_4$en)Cl$_2$, for which the first solvolysis reaction (k_{-2}) is the rate-determining step [7]. The kinetic data measured under such conditions are summarized in Table 2. A comparison of the k_{-2} values obtained in this way with the k_a values reported in Table 1 for the second substitution process, indicates that only in the case of the en complex is k_a a composite value, i.e. $k_a = k_{-1} + k_{-2}$ (see ref. 7). In the two other cases the agreement is rather good and indicates that $k_a = k_{-2}$. A summary of all the rate and activation parameters for the reactions in (1) is given in Table 3.

The introduction of substituents on the ethylenediamine ligand causes a significant decrease in k_1, which is accompanied by an increase in $\Delta H^{\neq}$ and $\Delta S^{\neq}$. A similar trend was reported before for a series of substitution reactions of sterically crowded dien complexes [1–5]. The significant decrease in k_1 is ascribed to the effect of steric crowding that affects

TABLE 1. Rate data for the complex formation of Pd(R$_4$en)(H$_2$O)$_2^{2+}$ with chloride ions according to the reactions outlined in (1)[a]

Investigated reaction	λ (nm)	pH	Temperature (°C)	[Cl$^-$] × 10^3 (M)	k_{obs}[b] (s^{-1})	k_a (s^{-1})	k_b (M^{-1} s^{-1})
Pd(en)(H$_2$O)$_2^{2+}$ + Cl$^-$ $\rightleftharpoons$ Pd(en)(H$_2$O)Cl$^+$ + H$_2$O[c]	370	3.5	12.4	5.0	79 ± 7	−1 ± 10	(1.6 ± 0.2) × 10^4
				6.0	102 ± 16		
				7.0	113 ± 13		
				8.0	130 ± 11		
			18.7	5.0	111 ± 8	−2 ± 13	(2.3 ± 0.2) × 10^4
				6.0	138 ± 11		
				7.0	152 ± 6		
				8.0	182 ± 9		
			25.0	5.0	135 ± 12	0 ± 9	(2.9 ± 0.1) × 10^4
				6.0	167 ± 9		
				6.25	170 ± 10		
				7.5	204 ± 18		
				8.0	225 ± 12		
Pd(en)(H$_2$O)Cl$^+$ + Cl$^-$ $\rightleftharpoons$ Pd(en)Cl$_2$ + H$_2$O[c,d]	370	4.9	15.0	7.5	12.0 ± 1.0	7.8 ± 0.3	618 ± 10
				15	16.8 ± 0.3		
				25	24.0 ± 1.0		
				50	38 ± 3		
			25.0	10	29 ± 1	15.7 ± 0.8	1340 ± 20
				20	43 ± 1		
				30	56 ± 1		
				40	68 ± 1		
				50	83 ± 3		
			35.0	7.5	52 ± 5	31 ± 4	2700 ± 150
				15	67 ± 3		
				25	104 ± 4		
				50	165 ± 5		
Pd(Me$_4$en)(H$_2$O)$_2^{2+}$ + Cl$^-$ $\rightleftharpoons$ Pd(Me$_4$en)(H$_2$O)Cl$^+$ + H$_2$O	345	3.8	16.0	6.0	65 ± 2	8 ± 8	(9.75 ± 0.08) × 10^3
				8.0	83 ± 2		
				10	112 ± 4		
				12	127 ± 3		
				15	151 ± 5		
			20.5	6.0	72 ± 1	2 ± 2	(1.27 ± 0.02) × 10^4
				8.0	99 ± 3		
				10	121 ± 5		
				12	149 ± 2		
				15	179 ± 4		
			25.0	6.0	90 ± 2	5 ± 5	(1.47 ± 0.04) × 10^4
				8.0	122 ± 3		
				10	155 ± 9		
				12	181 ± 2		
				15	223 ± 3		
Pd(Me$_4$en)(H$_2$O)Cl$^+$ + Cl$^-$ $\rightleftharpoons$ Pd(Me$_4$en)Cl$_2$ + H$_2$O[e]	345	3.8	16.0	8.0	2.98 ± 0.06	1.72 ± 0.04	157 ± 1
				10	3.26 ± 0.06		
				12	3.45 ± 0.08		
				15	4.09 ± 0.12		
				20	4.87 ± 0.14		
			20.5	8.0	3.68 ± 0.05	2.06 ± 0.07	206 ± 7
				10	4.10 ± 0.07		
				12	4.57 ± 0.10		
				15	5.13 ± 0.08		
				20	6.16 ± 0.12		
			25.0	8.0	5.19 ± 0.20	2.92 ± 0.10	286 ± 8
				10	5.89 ± 0.18		
				12	6.37 ± 0.10		
				15	7.19 ± 0.40		
				20	8.59 ± 0.14		
			30.1	8.0	7.75 ± 0.10	4.9 ± 0.4	362 ± 38
				10	8.58 ± 0.50		
				12	9.20 ± 0.17		
				15	10.1 ± 0.2		
				20	12.1 ± 0.3		

(*continued*)

TABLE 1. (*continued*)

Investigated reaction	λ (nm)	pH	Temperature (°C)	$[Cl^-] \times 10^3$ (M)	k_{obs}[b] (s^{-1})	k_a (s^{-1})	k_b ($M^{-1}\ s^{-1}$)
			38.7	8.0	14.3 ± 0.3	9.2 ± 0.6	609 ± 46
				10	14.7 ± 0.4		
				15	18.7 ± 0.3		
				20	21.3 ± 0.3		
$Pd(Et_4en)(H_2O)_2^{2+} + Cl^- \rightleftharpoons Pd(Et_4en)(H_2O)Cl^+ + H_2O$	360	3.0	14.9	6.0	5.3 ± 0.2	−0.4 ± 0.6	957 ± 46
				8.0	6.9 ± 0.3		
				12	11.3 ± 0.7		
				15	14.6 ± 0.7		
				20	18.3 ± 0.6		
			19.2	6.0	6.5 ± 0.2	−0.4 ± 0.2	1104 ± 143
				8.0	8.2 ± 0.2		
				12	13.1 ± 0.2		
				20	21.5 ± 0.3		
			25.0	6.0	10.3 ± 0.2	0.9 ± 1.3	1586 ± 96
				8.0	13.4 ± 0.2		
				12	19.5 ± 0.3		
				15	26.3 ± 0.8		
				20	31.9 ± 0.3		
			35.3	6.0	19.1 ± 0.3	1.4 ± 0.4	2951 ± 29
				8.0	24.9 ± 0.1		
				12	37.1 ± 0.4		
				20	60.4 ± 1.2		
$Pd(Et_4en)(H_2O)Cl^+ + Cl^- \rightleftharpoons Pd(Et_4en)Cl_2 + H_2O$[e]	360	3.0	14.9	6.0	0.199 ± 0.010	0.150 ± 0.006	7.8 ± 0.5
				8.0	0.215 ± 0.010		
				12	0.236 ± 0.004		
				15	0.272 ± 0.005		
				20	0.308 ± 0.020		
			19.2	6.0	0.272 ± 0.012	0.229 ± 0.007	9.0 ± 0.6
				8.0	0.312 ± 0.010		
				12	0.342 ± 0.010		
				20	0.404 ± 0.002		
			25.0	6.0	0.408 ± 0.010	0.320 ± 0.006	13.3 ± 0.5
				8.0	0.446 ± 0.007		
				12	0.488 ± 0.010		
				15	0.533 ± 0.008		
				20	0.599 ± 0.010		
			35.3	6.0	0.721 ± 0.008	0.540 ± 0.009	27.6 ± 0.7
				8.0	0.760 ± 0.020		
				12	0.865 ± 0.010		
				20	1.10 ± 0.01		

[a] $[Pd(II)] = (7–10) \times 10^{-4}$ M; ionic strength = 0.1 M. [b] Mean value of at least five kinetic experiments. [c] Data at 25 °C taken from ref. 7. [d] Reaction was measured starting with an equilibrated solution of $Pd(R_4en)Cl_2$. [e] Second reaction step observed when starting with $Pd(R_4en)(H_2O)_2^{2+}$.

the entrance of the chloride ion and accounts for the increase in $\Delta H^{\neq}$ with increasing crowding. A similar trend is observed for k_2 and k_{-2} in terms of a decrease in rate constant with increasing steric crowding, although this is accompanied by no specific trend in $\Delta H^{\neq}$ and a tendency to more negative values for $\Delta S^{\neq}$. The data in Table 3 demonstrate that k_2 is at least an order of magnitude smaller than k_1, which is in agreement with our observation that the two reaction steps can be quite easily separated kinetically. All the values of $\Delta S^{\neq}$ are remarkably negative and support the operation of an associative substitution process. The more negative values reported for $\Delta S^{\neq}$ associated with k_2 and k_{-2} for the more crowded complexes may result from specific solvation effects of the introduced substituents. Such a trend was not found for the detailed studies on the dien complexes [1–5], in which case only the rate constants and $\Delta H^{\neq}$ exhibited a meaningful trend with increasing steric hindrance. More work will have to be performed in order to clarify the peculiar trend observed in the $\Delta S^{\neq}$ values reported in this study. Obviously it will be appropriate to perform kinetic measurements at elevated pressure and to use $\Delta V^{\neq}$ rather than $\Delta S^{\neq}$ as a mechanistic parameter [1–5, 17].

The value of k_2 and k_{-2} can be used to calculate K_2 ($= k_2/k_{-2}$) and result in 138, 99 and 42 M^{-1} for

TABLE 2. Rate data for the solvolysis of $Pd(R_4en)Cl_2$ in the presence of base according to the overall scheme[a]

$$Pd(R_4en)Cl_2 + H_2O \xrightarrow{k_{-2}} Pd(R_4en)(H_2O)Cl^+ + Cl^-$$
$$\rightleftarrows$$
$$Pd(R_4en)(OH)Cl + H^+$$

R	$[OH^-]$ (M)	k_{obs}[b] (s^{-1})	k_{-2} (s^{-1})
H	0.025	9.6 ± 0.5	9.7 ± 0.8
	0.040	9.7 ± 0.5	
	0.050	9.7 ± 0.8	
Me	0.0125	2.8 ± 0.2	2.8 ± 0.2
	0.020	2.8 ± 0.1	
	0.025	2.8 ± 0.1	
	0.050	2.9 ± 0.4	
Et	0.0125	0.29 ± 0.01	0.29 ± 0.02
	0.020	0.29 ± 0.02	
	0.050	0.30 ± 0.02	

[a] $[Pd(II)] = (7–10) \times 10^{-4}$ M; temperature = 25.0 °C; ionic strength = 0.10 M. [b] Mean value of at least five kinetic runs.

R = H, Me and Et, respectively, which are in close agreement with the thermodynamic values reported above (viz. 130 ± 14, 105 ± 14 and 52 ± 9 M^{-1}, respectively). This trend clearly demonstrates that the stability of the dichloro complex decreases with increasing steric hindrance, i.e. the complex formation reaction is decelerated more than the reverse aquation reaction on increasing the steric hindrance. It should however be noted that the overall effect on K_1 and K_2 is not very large (only a factor of 2) which indicates that steric crowding has a very similar effect in terms of orders of magnitude on both the forward and reverse reactions.

At this point it is of interest to compare our findings with those of related studies. First of all the formation constants K_1 and K_2 reported in this study exhibit a decrease with increasing steric hindrance on the en ligand. A similar study of the spontaneous solvolysis reactions of complexes of the type $Pd(R_5dien)Cl^+$ [1, 18] indicated a gradual increase in dien complex formation constants with increasing steric hindrance. This difference may result from the fact that the steric hindrance on the dien ligand is closer to the actual substitution site than in the case of the en ligands, such that it can affect the kinetics of the forward and reverse reactions in a different way. This is also seen in a comparison of the anation rate constants. k_1 and k_2 in the present study (see Table 3) decrease by approximately one order of magnitude on going from the Me_4en to the Et_4en complex, whereas a decrease of three orders of magnitude was reported for the anation of

TABLE 3. Summary of rate and activation parameters for the reaction scheme[a]

$$Pd(R_4en)(H_2O)_2^{2+} + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pd(R_4en)(H_2O)Cl^+ + H_2O$$

$$Pd(R_4en)(H_2O)Cl^+ + Cl^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Pd(R_4en)Cl_2 + H_2O$$

R	k_1[b] (M^{-1} s^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	k_2[b] (M^{-1} s^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	k_{-2}[b] (s^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})
H	$(2.9 \pm 0.1) \times 10^4$	29 ± 2	−61 ± 7	1340 ± 20	52 ± 1	−10 ± 2	15.7 ± 0.8[c] 9.7 ± 0.1[d]	48 ± 1	−59 ± 2
Me	$(14.7 \pm 0.4) \times 10^3$	33 ± 2	−55 ± 7	286 ± 8	42 ± 1	−57 ± 4	2.9 ± 0.1 2.8 ± 0.1[d]	55 ± 4	−50 ± 14
Et	$(1.6 \pm 0.1) \times 10^3$	41 ± 3	−45 ± 10	13.3 ± 0.5	47 ± 4	−66 ± 15	0.32 ± 0.01 0.29 ± 0.01[d]	40 ± 4	−120 ± 13

[a] Data reported for ionic strength 0.10 M. [b] Data reported for 25 °C, see Table 1. [c] Composite rate constant, $k_a = k_{-1} + k_{-2}$ (see Discussion in ref.7). [d] Determined via base hydrolysis reaction, data from Table 2.

$Pd(Me_4dien)H_2O^{2+}$ and $Pd(Et_4dien)H_2O^{2+}$ [18]. Finally the values of K_1 and K_2 for the $Pd(R_4en)$ complexes are very close to those reported for the corresponding $Pt(NH_3)_2$ system, viz. $K_1 = 3700$ and $K_2 = 99$ M^{-1} [19], which suggests a very similar equilibrium situation for the latter system to that found for the $Pd(R_4en)$ complexes.

We conclude that most of the observed trends in the thermodynamic and kinetic data reported in this paper can be accounted for in terms of the effect of steric crowding. Electronic effects of the introduced substituents may account for small variations in the acid dissociation constants of the aqua complexes. It follows that steric crowding can be used to kinetically tune the reactivity of such model square planar complexes, an aspect which may have important implications for the antitumor activity of such species.

Acknowledgements

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and a loan of palladium chloride from HERAEUS GmbH, Hanau, F.R.G.

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