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Kinetic Studies on the Closure of a Chelate Ring in [(2-Dimethylaminoethyl)dimethylammonium]- and [(3-Dimethylaminopropyl)dimethylammonium]-trichloroplatinum(II) Complexes

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The title complexes, $[PtCl_3(Me_4\text{-Hen})]$ and $[PtCl_3(Me_4\text{-Hpn})]$ [Me_4-Hen = (2-dimethylaminoethyl)dimethylammonium, Me_4-Hpn = (3-dimethylaminopropyl)dimethylammonium], with the diamine ligand acting as unidentate, have been prepared and the kinetics of closure of the chelate ring studied in aqueous solution. The rate constants of the reaction $[PtCl_3(N{-}N)]^- \longrightarrow [PtCl_2(N{-}N)] + Cl^-$ ($N{-}N$ = Me_4en or Me_4pn), measured in basic medium at 25 °C, were k^f_{Cl} = 183 ± 6 (Me_4en) and 1.00 ± 0.03 s^{-1} (Me_4pn); temperature-variation studies gave $\Delta H^\ddagger$ = 43 ± 3 (Me_4en) and 57 ± 2 kJ mol^{-1} (Me_4pn), and $\Delta S^\ddagger$ = −49 ± 4 (Me_4en) and −46 ± 3 J K^{-1} mol^{-1} (Me_4pn). These data are interpreted as a measure of the greater conformational stability of the five- *versus* six-membered ring. The presence of two methyl substituents on the N atoms causes a 50—100-fold rate enhancement which is a measure of the so called ' Thorpe–Ingold ' or ' *gem*-dimethyl ' effect. Kinetic measurements at $pH < 7$ are interpreted according to a reaction mechanism in which reversible solvolysis of a *cis* chloride from the ring-opened species leads to two parallel paths for ring closure. The kinetic constants for acid hydrolysis [k_1 = (9.5 ± 0.5) × 10^{-4} (Me_4en) and (5.7 ± 0.2) × 10^{-4} s^{-1} (Me_4pn)] and chloride anation of the solvento-species [k_{-1} = 0.36 ± 0.01 (Me_4en) and 0.14 ± 0.01 dm^3 mol^{-1} s^{-1} (Me_4pn)] are in the usual range; the products of the acid-dissociation constant of semidetached (*i.e.* monoco-ordinated bidentate ligand) diamine and the kinetic constant of ring closing, in the chloro- and in the solvento-species are: $K^a_{Cl}k^f_{Cl}$ = (7.8 ± 0.4) × 10^{-7} (Me_4en) and (3.4 ± 0.3) × 10^{-10} (Me_4pn), and $K^a_{H_2O}k^f_{H_2O}$ = (1.03 ± 0.05) × 10^{-5} (Me_4en) and (1.4 ± 0.1) × 10^{-9} mol dm^{-3} s^{-1} (Me_4pn). From data in acidic and basic media, the acid-dissociation constant was calculated as K^a_{Cl} = 4.3 × 10^{-9} (Me_4en) and 3.4 × 10^{-10} mol dm^{-3} (Me_4pn), intermediate between those of the di- and mono-protonated free diamine.

THE chelate effect has been studied for a long time in connection with equilibrium constants of complex formation [1] and more recently attempts have been made to investigate the chelate effect from a kinetic point of view by measuring the rates of ring opening and ring closing in metal complexes of multidentate ligands.

In the case of square-planar complexes, kinetic studies on the closure of five-membered chelate rings have been performed for *trans*-$[PtCl_2(en{\cdot}HCl)_2]$,[2] $[PtCl_2(bama{\cdot}HCl)]$ and $[PtCl_2(taa{\cdot}2HCl)]$,[3] $[PtCl_3(Hbas{\cdot}HCl)]$ and $[PtCl_2(bas{\cdot}HCl)]$ [4] [en = 1,2-diaminoethane, bama = bis(2-aminoethyl)methylamine, taa = tris(2-aminoethyl)amine, and bas = bis(2-aminoethyl) sulphide]. Both the acid-dissociation constant of the semidetached (*i.e.* monoco-ordinated bidentate ligand) 2-aminoethyl group and the kinetic constant of ring closing were determined. The reverse (ring-opening) reaction could not be studied in these systems owing to the high stability of the chelate complexes. The opening and closing of chelate rings of different size were studied kinetically in *cis*-$[PtCl_2(dmso)(en{\cdot}HCl)]$,[5] *cis*-$[PtCl_2(dmso)(pn{\cdot}HCl)]$, and *cis*-$[PtCl_2(dmso)(bn{\cdot}HCl)]$ [6] (dmso = dimethyl sulphoxide, pn = 1,3-diaminopropane, and bn = 1,4-diaminobutane), however, with the exception of the bn complex, the experimental data did not allow the separation of the acid-dissociation equilibrium constant and the ring-closing kinetic constant. The same limitation also applies to the kinetic study of ring closure in *trans*-$[PtCl_2(en{\cdot}HCl)(NH_3)]$ and *trans*-$[PtCl_2(pn{\cdot}HCl)(NH_3)]$.[7]

The establishment of an equilibrium between a chelated substrate and a species containing a semi-detached ligand is also the first stage in the displacement of polyamines from reactive palladium(II) and gold(III) species, however this step is usually too fast to be followed kinetically and only a rough estimation of the product of the acid-dissociation equilibrium constant and ring-closing kinetic constant can be given.[8,9]

In this paper we report a complete kinetic study of the ring-closing process in $[PtCl_3(Me_4\text{-Hen})]$ and $[PtCl_3(Me_4\text{-Hpn})]$. The significance of the ring size and of the methyl substituents on the N atoms upon the rate of ring closing will be discussed.

EXPERIMENTAL

Commercial reagent-grade chemicals were used without further purification.

Preparations.—*Trichloro*[(*2-dimethylaminoethyl*)*dimethylammonium*]*platinum*(II). A white solution of $[Pt(C_2H_4)Cl(Me_4en)][ClO_4]$ [10] (0.2 g, 0.42 mmol) in concentrated hydrochloric acid (5 cm^3) was kept at room temperature for some days during which time it became orange-yellow; then, by slow concentration in a desiccator containing concentrated sulphuric acid and a beaker of potassium hydroxide pellets, it yielded large reddish crystals of the desired product. These were washed with methanol and air dried. The compound is insoluble in acetone and chlorinated solvents, and slightly soluble in water {Found: C, 18.9; H, 4.2; Cl, 21.2; N, 5.5. $[PtCl_3(Me_4\text{-}Hen)]$ requires C, 18.8; H, 4.15; Cl, 20.8; N, 5.5%}.

Trichloro[(3-dimethylaminopropyl)dimethylammonium]platinum(II) was prepared in a similar way using $[Pt(C_2H_4)Cl_2(Me_4\text{-}Hpn)][ClO_4]$ as starting substrate [11] {Found: C, 19.2; H, 4.3; Cl, 24.3; N, 6.2. $[PtCl_3(Me_4\text{-}Hpn)]$ requires C, 19.4; H, 4.4; Cl, 24.6; N, 6.5%}.

Kinetics.—Rate data were obtained spectrophotometrically by measuring changes of absorbance with time. First-order rate constants were calculated from plots of $\ln(A_t - A_\infty)$ 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.

Experiments at constant chloride concentration were carried out in 1-cm quartz cells using a complex concentration of 10^{-3} mol dm^{-3}. Experiments at negligible chloride concentration for measuring the rates of acid hydrolysis in the starting substrate and ring closing in the solvento-species were performed in a 10-cm quartz cell using a complex concentration of 10^{-4} mol dm^{-3}, under which conditions the equilibrium between chloro- and solvento-species is completely shifted towards the solvento-species. The same procedure was used to obtain the initial solution of solvento-complex to measure the rate of chloride anation.

Fast kinetic measurements in basic media were performed on a Durrum D-110 stopped-flow instrument by rapid mixing of a solution of the reactant substrate in HCl (0.05 mol dm^{-3}) and NaCl (0.05 mol dm^{-3}) with a second solution containing NaCl (0.10 mol dm^{-3}) and $Na_3[PO_4]$ (0.10 mol dm^{-3}), the resulting pH being *ca.* 11.5.

Kinetic measurements at pH <7.2 were performed on a Perkin-Elmer 475 spectrophotometer using $HClO_4$ for adjusting the pH to 0.7, phosphoric acid–sodium dihydrogenphosphate buffers for pH values in the range 0.7—3.2, and sodium dihydrogenphosphate–disodium hydrogenphosphate for pH values in the range 5.5—7.2.

TABLE 1

Values of $k_{obs.}$ for the reaction $[PtCl_2(Me_4\text{-}Hen)(OH_2)]^+ + Cl^- \longrightarrow [PtCl_3(Me_4\text{-}Hen)]$ in water at $I = 0.2$ mol dm^{-3} ($Na[ClO_4]$) and 25.0 °C

$[H^+]$/mol dm^{-3}	$10^2[Cl^-]$/mol dm^{-3}	$10^2k_{obs.}$/s^{-1}
0.20	0.50	0.360
	1.00	0.508
	2.00	0.865
	3.33	1.39
	5.00	1.94
	6.67	2.54
	8.33	3.23
	10.0	3.80

The pH was measured with a E-500 digital pH meter using a glass electrode, the instrument being calibrated with an equimolar H_3PO_4–NaH_2PO_4 buffer solution. The ionic strength was adjusted to a constant value with sodium perchlorate.

The experimentally determined rate constants, $k_{obs.}$/s^{-1}, are reported in Tables 1—5.

TABLE 2

Values of $k_{obs.}$ for the reaction $[PtCl_2(Me_4\text{-}Hpn)(OH_2)]^+ + Cl^- \longrightarrow [PtCl_3(Me_4\text{-}Hpn)]$ in water at $I = 0.3$ mol dm^{-3} ($Na[ClO_4]$) and 25.0 °C

$[H^+]$/mol dm^{-3}	$10^2[Cl^-]$/mol dm^{-3}	$10^2k_{obs.}$/s^{-1}
0.20	0.216	0.948
	1.54	2.84
	2.31	3.97
	3.00	4.81
	4.62	6.84
	6.67	10.0
	10.0	14.6

TABLE 3

Values of $k_{obs.}$ for the reaction $[PtCl_3(Me_4\text{-}Hen)] \longrightarrow [PtCl_2(Me_4en)] + H^+ + Cl^-$ in water at $I = 0.2$ mol dm^{-3} ($Na[ClO_4]$) and 25.0 °C

$[Cl^-]$/mol dm^{-3}	$10^{-2}[H^+]^{-1}$/dm^3 mol^{-1}	$10^4k_{obs.}$/s^{-1}
0.00	0.05	0.562
	0.17	1.95
	0.49	4.93
	0.87	8.55
	1.18	12.1
	1.51	15.5
	2.24	23.2
0.01	0.10	0.41
	0.31	0.90
	0.50	1.39
	0.95	2.64
	1.32	3.36
	1.32	3.39
	2.09	4.34
	2.75	5.75
	4.37	8.04
	4.57	8.72
	5.01	8.61
	7.41	11.9
	8.51	13.2
	11.2	16.0
	14.1	18.6
	14.5	18.4
0.10	0.83	1.13
	1.23	1.51
	2.09	2.22
	2.88	3.39
	4.79	4.74
	7.59	7.38
	9.55	9.39
	15.5	14.8

TABLE 4

Values of $k_{obs.}$ for the reaction $[PtCl_3(Me_4\text{-}Hpn)] \longrightarrow [PtCl_2(Me_4pn)] + H^+ + Cl^-$ in water at $I = 0.3$ mol dm^{-3} ($Na[ClO_4]$) and 25.0 °C

$[Cl^-]$/mol dm^{-3}	$10^{-6}[H^+]^{-1}$/dm^3 mol^{-1}	$10^4k_{obs.}$/s^{-1}
0.00	0.302	3.70
	0.537	5.89
	0.661	7.46
	1.58	12.5
	2.45	17.6
	3.09	17.9

TABLE 4 (*continued*)

$[Cl-]$ / mol dm^{-3}	$10^{-6}[H^+]^{-1}$ / dm^3 mol^{-1}	$10^4{}_{obs.}$ / s^{-1}
	5.62	21.2
	8.91	21.5
	11.7	25.0
	14.5	25.7
	14.8	26.1
0.10	1.23	4.78
	2.09	8.12
	2.63	9.57
	4.17	15.2
	5.00	18.6
	5.37	19.7
	7.24	24.0
	9.77	29.9

TABLE 5

Values of $k_{obs.}$ and activation parameters for ring-closing reactions measured in basic medium (I = 0.3 mol dm^{-3})

Complex	θ_c / °C	$k_{obs.}$ / s^{-1}	$\Delta H^‡$ / kJ mol^{-1}	$\Delta S^‡$ / J K^{-1} mol^{-1}
$[PtCl_3(Me_4en)]^-$	16.0	96	43 ± 3	−(49 ± 5)
	25.5	190		
	35.5	324		
$[PtCl_3(Me_4pn)]^-$	16.0	0.45	57 ± 2	−(46 ± 3)
	25.0	1.00		
	37.2	2.48		

RESULTS

Kinetics of Acid Hydrolysis and Chloride Anation.—Operating at low pH ($[H^+]$ = 0.20 mol dm^{-3}) it is possible to suppress the ring-closing reaction and measure the rate of substitution of a chloride by a water molecule in the starting substrate with formation of a solvento-species. Since chloride ion is released in the reaction it was necessary to operate at a low concentration of complex ($\leqslant 10^{-4}$ mol dm^{-3}) in order to ensure complete hydrolysis; under these conditions, good linear semilogarithmic plots and first-order kinetics were obtained [equation (1)]. Only one

$$k_{obs.} = k_1 \tag{1}$$

chloride ion *cis* to the nitrogen ligand was substituted by a water molecule and this was confirmed by performing the ring-closing reaction on the solvento-species and analyzing the product which was always $[PtCl_2(N-N)]$ (N–N = Me_4en or Me_4pn).

The anation reaction was studied by adding sodium chloride to a solution of the solvento-species and following the spectral changes. Using enough chloride ion to ensure pseudo-first-order conditions, good linear semilogarithmic plots were obtained. Plots of $k_{obs.}$ against $[Cl^-]$ were linear and had a discrete intercept the value of which agreed, within the limits of experimental error, with the rate constants of acid hydrolysis measured in independent experiments [Figure 1, equation (2)].

$$k_{obs.} = k_1 + k_{-1}[Cl^-] \tag{2}$$

The values of the intercepts, k_1/s^{-1}, and of the gradients, $k_{-1}/dm^3\ mol^{-1}\ s^{-1}$, were calculated from least-squares fits and quoted uncertainties (Table 6) are 95% confidence limits.

Kinetics of the Closure of the Five-membered Ring in Acidic Media.—The rate of ring closing in acidic media ($0.7 \leqslant$ pH $\leqslant 3.2$) of $[PtCl_3(Me_4\text{-}Hen)]$ was a function of the hydrogen- and chloride-ion concentrations.

Starting from the solvento-species, *cis*-$[PtCl_2(Me_4\text{-}Hen)(OH_2)]^+$, and in the absence of added chloride, the spectrum changed to that of $[PtCl_2(Me_4en)]$ at a rate which depended upon the pH of the solution. A plot of $k_{obs.}$ against $[H^+]^{-1}$ was linear and passed through the origin [curve (*a*) of Figure 2, equation (3)]; the slope of this plot, $k^f{}_{H_2O}K^a{}_{H_2O}$/mol dm^{-3} s^{-1} (the reason for this choice of symbolism will appear clear in the Discussion section), derived from a least-squares analysis of the primary data is given in Table 6.

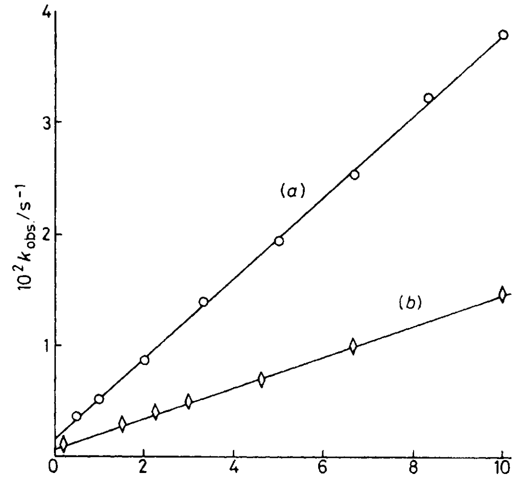


FIGURE 1 Plot of $k_{obs.}$ against $[Cl^-]$ for the reaction: $[PtCl_2(N-NH)(OH_2)]^+ + Cl^- \longrightarrow [PtCl_3(N-NH)]$, N–N = Me_4en (*a*) and Me_4pn (*b*); $[H^+]$ = 0.20, I = 0.20 (*a*) and 0.30 (*b*) mol dm^{-3} ($Na[ClO_4]$), 25.0 °C

$$k_{obs.} = k^f{}_{H_2O}K^a{}_{H_2O}[H^+]^{-1} \tag{3}$$

Starting from the chloro-species and in the presence of added chloride, the ring-closing process occurred at a rate which depended upon the hydrogen- and chloride-ion concentrations. However, at constant $[Cl^-]$, a plot of $k_{obs.}$ against $[H^+]^{-1}$ was not linear and the curvature became less pronounced as the chloride concentration was increased [curves (*b*) and (*c*) of Figure 2]. This leads to a reaction mechanism in which the acid hydrolysis and chloride anation, and the ring closing in the chloro- and solvento-species, occur simultaneously (Scheme 1).

From this set of first-order reactions, and without

TABLE 6

Values of kinetic and equilibrium constants measured at 25.0 °C

Constant	Complexes	
	$[PtCl_3(Me_4\text{-}Hen)]$ [a]	$[PtCl_3(Me_4\text{-}Hpn)]$ [b]
k_1/s^{-1}	$(9.5 \pm 0.5) \times 10^{-4}$	$(5.7 \pm 0.1) \times 10^{-4}$
$k_{-1}/dm^3\ mol^{-1}\ s^{-1}$	0.36 ± 0.01	0.14 ± 0.01
$k^f{}_{H_2O}K^a{}_{H_2O}$/ mol dm^{-3} s^{-1}	$(1.03 \pm 0.05) \times 10^{-5}$	$(1.4 \pm 0.1) \times 10^{-9}$
$K^i{}_{H_2O}$/mol dm^{-3}	*c*	$(4.7 \pm 0.5) \times 10^{-7}$
$k^f{}_{Cl}K^a{}_{Cl}$/ mol dm^{-3} s^{-1}	$(7.8 \pm 0.4) \times 10^{-7}$	$(3.4 \pm 0.3) \times 10^{-10}$
$k^f{}_{Cl}/s^{-1}$	183 ± 10	1.00 ± 0.05
$K^a{}_{Cl}$/mol dm^{-3}	4.3×10^{-9}	3.4×10^{-10}

[a] I = 0.2 mol dm^{-3} ($Na[ClO_4]$). [b] I = 0.3 mol dm^{-3} ($Na[ClO_4]$). [c] Under the experimental conditions used, $K^i{}_{H_2O}[H^+]^{-1}$ was negligible and could not be determined.

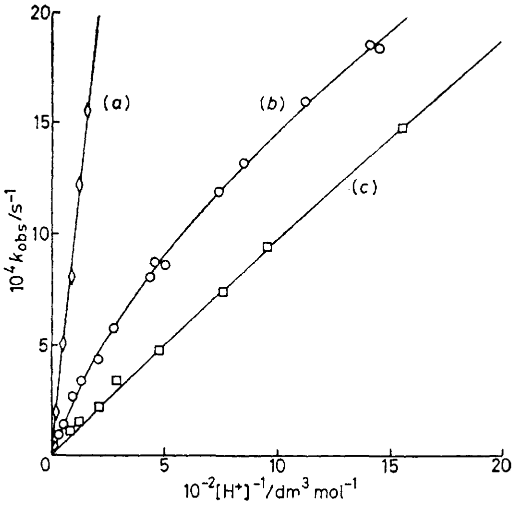
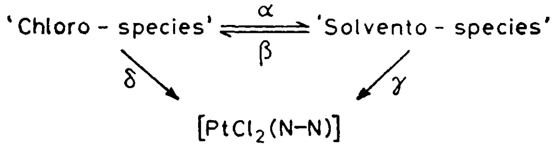


FIGURE 2 Plot of $k_{obs.}$ against $[H^+]^{-1}$ for the reactions $[PtCl_2(Me_4\text{-}Hen)(OH_2)]^+ \longrightarrow [PtCl_2(Me_4en)] + H^+ + H_2O$ (*a*) and $[PtCl_3(Me_4\text{-}Hen)] \longrightarrow [PtCl_2(Me_4en)] + H^+ + Cl^-$ at $[Cl^-] = 0.01$ (*b*) and 0.10 mol dm^{-3} (*c*). $I = 0.20$ mol dm^{-3} (Na[ClO$_4$]), 25.0 °C

adopting either the approximation of a pre-equilibrium between the chloro- and solvento-species $[(\delta - \gamma)(\alpha + \beta)^{-1} \approx 0]$ or that of a steady state for the solvento-species $[(\alpha,\delta)(\beta + \gamma)^{-1} \approx 0]$, equation (4) for the $k_{obs.}$ of the slower process is obtained.[12] Using equation (4) and substituting

$$k_{obs.} = \tfrac{1}{2}\{(\alpha + \beta + \gamma + \delta) - [(\alpha + \beta)^2 + (\delta - \gamma)^2 + 2(\alpha - \beta)(\delta - \gamma)]^{\frac{1}{2}}\} \quad (4)$$

for α, β, and γ the expressions for $k_{obs.}$ of (1), (2), and (3) respectively, it is possible to derive δ [equation (5)] by a non-linear least-squares curve-fitting procedure. The value of $k^f_{Cl}K^a_{Cl}$/mol dm^{-3} s^{-1} is reported in Table 6.



SCHEME 1

$$\delta = k^f_{Cl}K^a_{Cl}[H^+]^{-1} \quad (5)$$

It can be shown that under our experimental conditions neither approximation, of a pre-equilibrium or of a steady state, leads to an accurate fitting of the experimental data.

Kinetics of the Closure of the Six-membered Ring in Acidic Media.—The ring-closing process in $[PtCl_3(Me_4\text{-}Hpn)]$ was studied at lower acidity ($5.5 < pH < 7.2$) than that used in $[PtCl_3(Me_4\text{-}Hen)]$ ($0.7 < pH < 3.2$) in order to have measurable rates.

Starting from the solvento-species and in the absence of added chloride, the dependence of the observed rate constant upon $[H^+]^{-1}$ was more complicated than the linear relationship observed for the Me$_4$en complex [curve (*a*) of Figure 3]. However, a plot of $1/k_{obs.}$ against $[H^+]$ was linear and had a discrete intercept; this is consistent with a relationship of the form (6) where $(k^f_{H_2O}K^a_{H_2O})^{-1}$/s dm^3 mol^{-1}

$$k_{obs.} = k^f_{H_2O}K^a_{H_2O}[H^+]^{-1}\{1/(1 + K^i_{H_2O}[H^+]^{-1})\} \quad (6)$$

and $K^i_{H_2O}(k^f_{H_2O}K^a_{H_2O})^{-1}$/s are the slope and the intercept respectively (their values, derived from a linear least-squares analysis of the primary data, are reported in Table 6). The most simple explanation for the different behaviour of the Me$_4$en and the Me$_4$pn complex [equations (3) and (6) respectively] is that at the lower acidity used in the latter case the solvento-species, *cis*-$[PtCl_2(Me_4\text{-}Hpn)(OH_2)]^+$, undergoes extensive dissociation to give the hydroxo-species *cis*-$[PtCl_2(OH)(Me_4\text{-}Hpn)]$, which is unreactive towards ring closing [equation (7)].

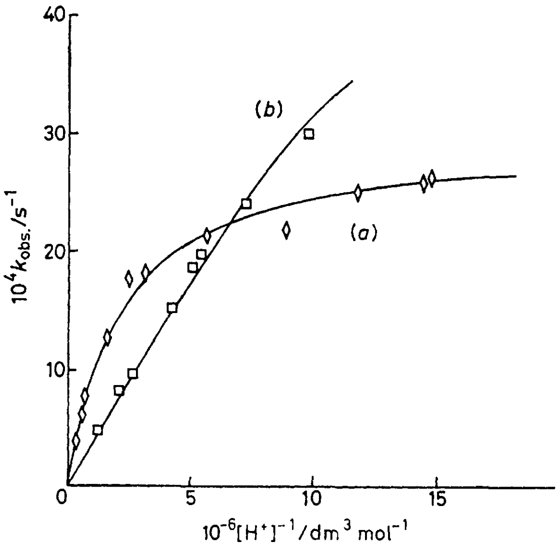


FIGURE 3 Plot of $k_{obs.}$ against $[H^+]^{-1}$ for the reactions $[PtCl_2(Me_4\text{-}Hpn)(OH_2)]^+ \longrightarrow [PtCl_2(Me_4pn)] + H^+ + H_2O$ (*a*) and $[PtCl_3(Me_4\text{-}Hpn)] \longrightarrow [PtCl_2(Me_4pn)] + H^+ + Cl^-$ at $[Cl^-] = 0.10$ mol dm^{-3} (*b*). $I = 0.30$ mol dm^{-3} (Na[ClO$_4$]), 25.0 °C

$$cis\text{-}[PtCl_2(Me_4\text{-}Hpn)(OH_2)]^+ \overset{K^i_{H_2O}[H^+]^{-1}}{\rightleftharpoons} cis\text{-}[PtCl_2(OH)(Me_4\text{-}Hpn)] \quad (7)$$

In order to check the validity of this assumption we have performed a kinetic run at pH 11, under which conditions the solvento-species is completely dissociated to the hydroxo-species. The estimated first-order rate constant (affected by a rather large error due to experimental difficulties arising from concurrent solvolysis reactions) was *ca.* 5×10^{-4} s^{-1} and possibly arises from a ring-closing reaction in the solvento-species still in equilibrium with the hydroxo-species and/or a ring-closing reaction in the hydroxo-species with displacement of the chloride *trans* to the hydroxyl group since we believe that, as usually found, the hydroxyl group is totally inert towards substitution.

Starting from the chloro-species and in the presence of added chloride the ring-closing process occurs at a rate which depends upon the hydrogen- and chloride-ion concentration [curve (*b*) of Figure 3]. Using equation (4) and substituting for α and γ the expressions for $k_{obs.}$ in (1) and (6) respectively and for β the expression for equation (3) multiplied by $1/(1 + K^i_{H_2O}[H^+]^{-1})$ to account for the formation, under the actual experimental conditions, of unreactive hydroxo-species, δ could be determined by a non-linear least-squares curve-fitting procedure [equation (5)]. The value of $k^f_{Cl}K^a_{Cl}$ so determined is reported in Table 6.

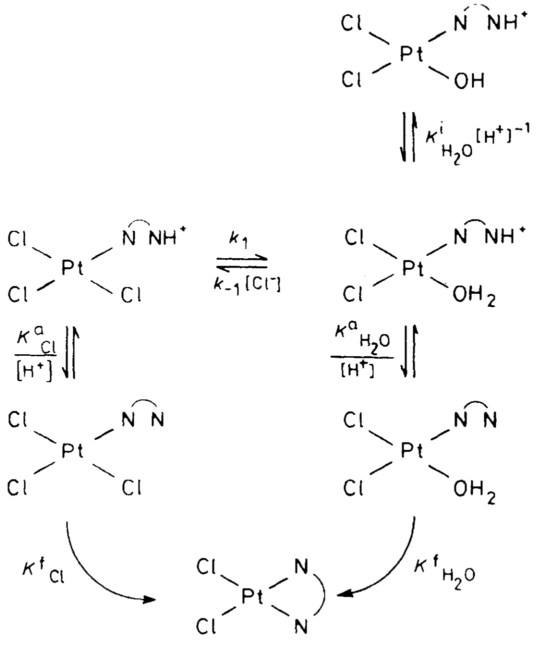
It is to be noted that the calculated values of $k^f_{Cl}K^a_{Cl}$

agreed within a 20% error with the slope of the quasi-linear curve (*c*) of Figure 2 and curve (*b*) of Figure 3 indicating that at $[Cl^-] = 0.10$ mol dm^{-3} the concentration, and the contribution to the total rate, of the chloro-species are predominant.

Kinetics of the Closure of the Five- and Six-membered Rings in Basic Media.—The ring-closing reactions were also studied under conditions where the pH was high enough for all the substrate to be in the form of the unprotonated ring-opened species. These reactions were fast enough to require the use of a stopped-flow apparatus. To ensure that the bulk of the substrate was in the form of the chloro-species, the starting complexes were dissolved in HCl (0.05 mol dm^{-3}) and NaCl (0.05 mol dm^{-3}) and the reaction initiated by mixing this solution with a solution of NaCl (0.10 mol dm^{-3}) and $Na_3[PO_4]$ (0.10 mol dm^{-3}), the resulting pH being 11.5. The rate constants were pH independent and their values (each the average from at least three independent determinations) measured at different temperatures are given in Table 5 with the calculated enthalpy and entropy of activation.

DISCUSSION

From the experimental data it is evident that a reversible solvolysis of the chloride from the ring-opened species leads to two parallel paths for ring closure; their dependence upon the pH is easily understood on the grounds that the free end of the diamine must be unprotonated in order to bond to platinum, that is the ring-closing step is preceded by a rapid acid-dissociation equilibrium. Moreover at pH $\geqslant 5.5$ (used for ring-closing reactions in the Me_4pn complex) the solvento-species undergoes acid dissociation with formation of the hydroxo-species which is unreactive towards ring closing. A straightforward reaction mechanism deduced from these data is depicted in Scheme 2.



SCHEME 2

The rate expression derived therefrom is given by equation (4) where α, β, γ, and δ are related to the kinetic constants by the following relationships, equations (8)—(11).

$$\alpha = k_1/(1 + K^a_{Cl}[H^+]^{-1}) \tag{8}$$

$$\beta = k_{-1}[Cl^-]/(1 + K^a_{H_2O}[H^+]^{-1} + K^i_{H_2O}[H^+]^{-1}) \tag{9}$$

$$\gamma = k^f_{H_2O}K^a_{H_2O}[H^+]^{-1}/(1 + K^a_{H_2O}[H^+]^{-1} + K^i_{H_2O}[H^+]^{-1}) \tag{10}$$

$$\delta = k^f_{Cl}K^a_{Cl}[H^+]^{-1}/(1 + K^a_{Cl}[H^+]^{-1}) \tag{11}$$

Under the experimental conditions of pH $\leqslant 3.2$, the terms $K^a[H^+]^{-1}$ and $K^i_{H_2O}[H^+]^{-1}$ are small compared to 1 and therefore equations (8)—(11) become identical to the experimentally determined equations (1), (2), (3), and (5) respectively. On the other hand, for pH values in the range 5.5—7.2 only the term $K^a[H^+]^{-1}$ can be neglected in the denominators of equations (8)—(11) and therefore equation (10) becomes identical to (6).

The rate constants measured in alkaline solutions and in the presence of excess of chloride can be directly assigned to k^f_{Cl}, neglecting any possible hydrolysis reaction since under these conditions the rate of ring closing is much greater than that of solvolysis. The independently determined values of k^f_{Cl} when combined with the values of $k^f_{Cl}K^a_{Cl}$ obtained from studies in acidic media allow the evaluation of K^a_{Cl}.

The first data of Table 6 to be discussed are the rate constants for acid hydrolysis (k_1/s^{-1}) and chloride anation (k_{-1}/dm^3 mol^{-1} s^{-1}). If we compare the data for the $[PtCl_3(Me_4\text{-}Hen)]$ and $[PtCl_3(Me_4\text{-}Hpn)]$ complexes with those for the analogous $[PtCl_3(NH_3)]^-$ ($k_1 = 5.6 \times 10^{-5}$ s^{-1} and $k_{-1} = 4.3 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}),[13] it appears that, while the equilibrium constants (k_1/k_{-1}) are very similar in the three cases (2.6×10^{-3}, 4.1×10^{-3}, and 1.3×10^{-3} mol dm^{-3} respectively) indicating a comparable *cis* influence of the three ligands ($Me_4\text{-}Hen^+$, $Me_4\text{-}Hpn^+$, and NH_3 respectively), the rate constants in the first two cases are a factor of ten higher than the third one. The *cis* effect of the three ligands can account for these differences; if we apply to the present case the equation derived for the basicity effect of the *cis* amine on chloride substitution by another amine molecule in *cis*-$[PtCl_2(dmso)](amine)$ complexes ($\log k = -0.4\ pK^a_{amine} + C$; k = rate constant for chloride substitution, dm^3 mol^{-1} s^{-1} and C = constant),[14] a ten-fold rate increase (going from NH_3 to $Me_4\text{-}Hpn^+$ and $Me_4\text{-}Hen^+$) is expected. Therefore, we exclude the existence of a neighbouring-group effect of the cationic end of the semi-detached diamine on the rates of these reactions, also on the grounds that this effect should be different for acid hydrolysis and chloride anation.

By comparing the rates of ring closing in the chloro- (k^f_{Cl}) and in the solvento-species ($k^f_{H_2O}$) the effect of the leaving group in these unimolecular processes could be studied. However, it was possible to measure directly only k^f_{Cl} and not $k^f_{H_2O}$, since in basic medium the solvento-species is converted immediately into the unreactive hydroxo-species. Therefore, we can only compare the products $k^f_{Cl}K^a_{Cl}$ and $k^f_{H_2O}K^a_{H_2O}$ and, since it is unlikely that the difference of only one ligand in the coordination sphere of platinum will have a significant effect on the basicity of the unco-ordinated end of the diamine, we can ascribe to k^f_{Cl} and $k^f_{H_2O}$ the differences observed in the products $k^f_{Cl}K^a_{Cl}$ and $k^f_{H_2O}K^a_{H_2O}$. With this assumption, the solvento-species appears to be more reactive than the chloro-species by factors of 13 and 4 for the Me_4en and Me_4pn complexes respectively. Data on the leaving-group effect, as measured by the $k^f_{H_2O}$: k^f_{Cl} ratio, relative to the entry of amines in platinum(II) substrates are scanty in the literature. A 54-fold greater substitutional lability was found in $[Pt(dien)(OH_2)]^{2+}$ relative to $[PtCl(dien)]^+$ [dien = bis(2-aminoethyl)amine] [15] while a 28-fold difference was found between $[Pt(C_2H_4)Cl_3]^-$ and $[Pt(C_2H_4)Cl_2(OH_2)]$.[16] For ring-closing reactions, a $k^f_{H_2O} : k^f_{Cl}$ ratio of 40 : 1 was reported for $[PtCl(dmso)(Hen)(OH_2)]^{2+}$ and $[PtCl_2(dmso)(Hen)]^+$,[5] while a value of 2 : 1 can be calculated for $[Pd(en)(Hen)(OH_2)]^{3+}$ and $[PdCl(en)(Hen)]^{2+}$.[8] It appears, therefore, that the leaving-group effect does not vary much regardless of whether the substitution is a bimolecular process or a unimolecular chelate-ring closure.

From the data in Table 6 it appears that the Me_4en complex undergoes ring closing much more readily than the Me_4pn complex, the ratio of k^f_{Cl} values being *ca.* $2 \times 10^2 : 1$. One can argue that this difference stems from the different basicity of the two amines, however we can also point out, without going into detail, that the basicity of the chelating diamine exerts its influence upon the reaction rate in opposite directions through the *cis* effect and the entering-group effect; therefore the net result will tend to be quite small. Moreover, as has already been envisaged, the basicity-related *cis* effect and the entering group effect of an amine operate mainly through the transition state; therefore in chelating diamines, since both nitrogens become attached to the same metal atom, it is reasonable to suggest that the dominant influence on the effective basicity involves the interactions of the two nitrogens with the metal, the length of the carbon chain serving only to modify the ligand ' bite ' and the orientation of the N substituents. As a consequence, the effective basicity of the nitrogens in these chelating diamines should remain roughly constant and therefore the different rates should reflect mainly the greater conformational stability of the five- *versus* six-membered rings.[17]

The activation entropies (Table 5) are more positive than those usually found for bimolecular substitution reactions in platinum(II) complexes (-60 to -130 J K^{-1} mol^{-1}) [18] and are consistent with an intramolecular process. Moreover, while the entropy is very similar for both complexes, the enthalpy of activation is lower by *ca.* 15 kJ mol^{-1} for the Me_4en complex than the Me_4pn complex. Therefore, the greater stability of the five- *versus* six-membered ring stems from a more favourable enthalpy rather than a more favourable entropy.[19]

It is well established that *gem*-dimethyl or similar groups cause a remarkable stabilization of small rings and also increase the rate at which small rings are formed. This is called the ' Thorpe–Ingold ' or ' *gem*-dimethyl ' effect.[20] It would therefore be of interest to observe the extent to which such a steric effect operates when an atom (platinum) much larger than carbon is involved. For this purpose we must compare the rates of ring closing in unsubstituted and *NN*-dimethyl substituted amines. Until now we have been unable to prepare complexes with unsubstituted en and pn ligands analogous to the ones reported in this work; however, we can calculate the rate of ring closing in a hypothetical $[PtCl_3(L–N)]^-$ complex [L–N being a L-bonded (2-aminoethyl)-L ligand] using the data of related complexes such as *trans*-$[PtCl_2(en)_2]$,[2] $[PtCl_2(bama)]$,[3] and $[PtCl_3(bas)]^-$,[4] all having an unco-ordinated 2-aminoethyl group. After correcting for the *cis*- and *trans*-effects of non-participating ligands other than chloride,[21] the values k^f_{Cl} 2.1, 3.5, and 3.6 s^{-1} are calculated from the data of the three complexes given above.

In spite of the gross approximation and the different nature of L, the agreement among the three calculated values is fairly good. If we compare these with the value of 183 s^{-1} measured for the Me_4en complex we must conclude that the ' *gem*-dimethyl ' groups cause a remarkable 50—100-fold increase in the rate constant. A similar conclusion can be drawn from comparison of ' effective molarity ' in unsubstituted and *NN*-dimethyl-substituted 2-aminoethyl complexes. The ' effective molarity ' of the free end of a monoco-ordinated bidentate ligand has been defined as the ratio between the first-order rate constant for ring closing and the second-order rate constant for chloride-ion substitution by ammonia in a strictly related complex. Without correcting for any basicity effect, an ' effective molarity ' of 1×10^3—4×10^3 mol dm^{-3} is always calculated for an unsubstituted 2-aminoethyl group in platinum complexes. On the other hand, the ratio between the rate of ring closing in $[PtCl_3(Me_4en)]^-$ and that of *cis*-chloride substitution by ammonia in $[PtCl_3(NH_3)]^-$ [22] is *ca.* 10^5 mol dm^{-3} which is 50—100 times higher than the usual value. This gives further support to our statement.

It is finally to be noted that the acid-dissociation constant of semidetached diamine, K^a_{Cl}, is intermediate between those of di- and mono-protonated free diamine [23] although the actual value is closer to the value for the latter. We also note that the acid-dissociation constant of the solvento-species to give the hydroxo-species, $K^i_{H_2O}$, is similar to that observed in *cis*-$[PtCl_2(OH_2)(NH_3)]$ ($K^i = 10^{-7}$ mol dm^{-3}).[24]

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