# Kinetics and Mechanism of the Reaction of Tetrachloroplatinum(II) with Propane-1,3-diamine

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The reaction of propane-1,3-diamine (pd) with $[PtCl_4]^{2-}$ proceeds in two stages. The first stage, formation of $[Pt(pd)Cl_2]$, is governed by the rate equation $k_{obs.,1} = k_{S,1} + k_{L,1}[pd]_T$. The rate constant $k_{S,1}$ corresponds to the rate of hydrolysis of $[PtCl_4]^{2-}$ and good agreement has been found with independent determinations of this rate constant. The hydrogen-ion dependence of $k_{L,1}$ is interpreted in terms of rate-determining attack on $[PtCl_4]^{2-}$ by both unprotonated and monoprotonated forms of the ligand. Activation parameters for these paths have been determined. The second stage of the reaction, formation of $[Pt(pd)_2]^{2+}$, is governed by the rate equation $k_{obs.,2} = k_{L,2}[pd]_T$, where the hydrogen-ion dependence of $k_{L,2}$ is similar to that of $k_{L,1}$. The kinetic data are discussed in the light of current views on the mechanism of substitution reactions at square-planar substrates, with special reference to the role of solvated intermediates.

STUDIES of the reactions of amines with platinum(II) complexes have played a considerable role in the elucidation of the mechanism of substitution reactions of these complexes. However, the vast majority of such studies has dealt with unidentate amines, and it is only recently that attention has been focused on the mode of reaction of multidentate amines with square-planar substrates. For platinum(II) complexes, the reactions of 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen) with $[PtX_4]^{2-}$ (X = Cl or Br) have been thoroughly investigated by Rund and his co-workers.[1–5] For phen, the observed kinetic behaviour was anomalous: a two-term rate law was observed in which both terms were first order in complex and ligand concentrations. In the more usual two-term rate expression (1) observed

$$\text{Rate} = (k_1 + k_2[\text{L}])[\text{Pt}^{II}] \qquad (1)$$

[1] F. A. Palocsy and J. V. Rund, *Inorg. Chem.*, 1969, **8**, 524.
[2] J. V. Rund and F. A. Palocsy, *Inorg. Chem.*, 1969, **8**, 2242.
[3] J. H. Cawley and J. V. Rund, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1406.
[4] D. E. Schwab and J. V. Rund, *Inorg. Chem.*, 1972, **11**, 499.
[5] J. V. Rund, *Inorg. Chem.*, 1974, **13**, 738.

for platinum(II) complexes [6] one term is independent of ligand concentration, which derives from rate-determining formation of a solvated complex * followed by rapid reaction with the ligand. The observed kinetics were attributed to parallel rate-determining attack of phen on both $[PtCl_4]^{2-}$ and $[PtCl_3(OH_2)]^-$, the latter species being formed in equilibrium (2) faster than its reaction with the ligand.[1,2,4]

$$[PtCl_4]^{2-} + H_2O \rightleftharpoons [PtCl_3(OH_2)]^- + Cl^- \quad (2)$$
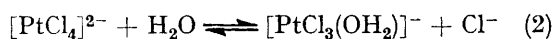
The reactions of 3-azapentane-1,5-diamine (dien) with a few platinum(II) substrates were investigated by Teggins and his co-workers.[7-9] With both $[PtCl_4]^{2-}$ and $[PtBr_4]^{2-}$, the kinetic behaviour deviated from (1), in that no term independent of the ligand concentration was observed.[7,8] This was explained in terms of the reaction of three ligand species, namely the neutral and mono- and di-protonated forms, with the same complex moiety, $[PtX_4]^{2-}$. Aqua-complexes were shown not to participate in the reaction. Work on other bi- or multi-dentate amines includes a number of studies with ethylenediamine (en) and propylenediamine (pn).[10-12] However, in these the effect of hydrogen-ion concentration was ignored and the question of the mechanistic role of solvated complexes was not investigated. It is surprising that detailed studies are lacking for the prototype square-planar system, $Pt^{II}$, whereas the reactions of en and its substituted congeners with $[PdCl_4]^{2-}$ and $[AuCl_4]^-$ have been thoroughly studied.[13-16] Palocsy and Rund [1] observed that the reactivities of the amines phen, bipy, and en towards $[PtCl_4]^{2-}$ are in the ratio 1 : 3 : 100. The reaction with en was not studied in detail, but it was suggested that the steric rigidity of phen and bipy contributed towards their low reactivities.

The present study of the mechanism of the interaction of propane-1,3-diamine (pd) with $[PtCl_4]^{2-}$, was undertaken in order to provide a quantitative basis for the comparison of the kinetic behaviour of phen and bipy, on the one hand, with that of an aliphatic diamine not subject to stringent stereochemical rigidity, on the other, as well as to determine the role of solvated species in the substitution reactions of chelating ligands.

## EXPERIMENTAL

Solutions of $K_2[PtCl_4]$ containing the appropriate amount of sodium chloride were made up to constant ionic strength ($I = 2.0$ mol dm$^{-3}$) with sodium perchlorate and allowed to equilibrate. The chloride concentration of solutions of propane-1,3-diamine dihydrochloride (pd·2HCl) was matched to that of the complex solutions with which they were allowed to react by addition of sodium chloride. Sodium

hydroxide was added until the desired pH was attained, and the ionic strength was adjusted ($I = 2.0$ mol dm$^{-3}$) with sodium perchlorate. The reaction was initiated by mixing appropriate volumes of complex and ligand solutions, previously equilibrated with respect to temperature in a stoppered cell. The reaction was monitored on a Perkin-Elmer 402 spectrophotometer, employing five-fold vertical-scale (absorbance) expansion throughout. The spectrophotometer was fitted with a thermostatted sample holder facilitating temperature control to ±0.1 K. In all reactions a large excess of ligand was used to ensure pseudo-first-order conditions. During the course of the reaction the pH changes were very small, and the pH of a given reaction was taken to be that measured when the reaction was approximately half-complete. Acidity constants were obtained from pH titration of 0.01 mol dm$^{-3}$ solutions of pd·2HCl with 0.05 mol dm$^{-3}$ solutions of sodium hydroxide, both made up to $I = 2.0$ mol dm$^{-3}$ with sodium perchlorate using a Radiometer model 26 pH meter.

Analytical grade sodium perchlorate and sodium chloride were recrystallised from triply distilled water which was used throughout. Propane-1,3-diamine dihydrochloride was prepared by addition of AnalaR hydrochloric acid to an aqueous solution of propane-1,3-diamine (Fluka, puriss grade) and evaporation of the solution on a water-bath until the salt just began to crystallise. On cooling, pd·2HCl was deposited and was recrystallised from ethanol–water mixtures. The complex $[Pt(pd)_2]Cl_2$ was prepared in a similar manner to the literature method [17] for $[Pt(en)_2]Cl_2$ and analysed satisfactorily. Spectra obtained on completion of kinetic runs were identical with those of solutions of $[Pt(pd)_2]Cl_2$ of the same concentration.

## RESULTS

On addition of pd to a solution of $[PtCl_4]^{2-}$, the absorption at the two absorption maxima of $[PtCl_4]^{2-}$, 394 and 335 nm, gradually decreased and isosbestic points developed at 360, 320, and 278 nm. The absorbance at all these wavelengths later decreased and the isosbestic points disappeared. When all spectral changes were complete, the final spectrum was identical to that of $[Pt(pd)_2]^{2+}$ prepared independently. The spectral changes can be attributed to the sequence $[PtCl_4]^{2-} \longrightarrow [Pt(pd)Cl_2] \longrightarrow [Pt(pd)_2]^{2+}$. In the early stages of the reaction, only the two species $[PtCl_4]^{2-}$ and $[Pt(pd)Cl_2]$ are present and this is reflected in the development of the isosbestic points. As the species $[Pt(pd)_2]^{2+}$ begins to be formed in significant amounts, the isosbestic points are destroyed and the absorbance at these wavelengths changes. The reaction was conducted at sufficiently low concentrations of the complex that the sparingly soluble $[Pt(pd)Cl_2]$ was not precipitated.

The rate of the first reaction was monitored by following the absorbance at 395 nm. Plots of log($A_t - A_\infty$) against time were linear and values of the pseudo-first-order

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[6] F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967.

[7] J. E. Teggins and T. S. Woods, *Inorg. Chem.*, 1968, **7**, 1424.

[8] J. E. Teggins, J. A. McCann, and E. D. Smith, *Inorg. Chem.*, 1970, **9**, 1294.

[9] E. D. Smith, J. A. McCann, and J. E. Teggins, *Inorg. Chem.*, 1969, **8**, 1872.

[10] L. Baracco, L. Cattalini, J. S. Coe, and E. Rotondo, *J. Chem. Soc. (A)*, 1971, 1517.

[11] Y. N. Kukushkin and U. B. Ukraintsev, *Zhur. neorg. Khim.*, 1968, **13**, 2886.

[12] Y. N. Kukushkin and U. B. Ukraintsev, *Zhur. neorg. Khim.*, 1972, **17**, 2687.

[13] W. J. Louw and W. Robb, *Inorg. Chim. Acta*, 1969, **3**, 29, 303, 307.

[14] P. van Z. Bekker, W. J. Louw, and W. Robb, *Inorg. Chim. Acta*, 1972, **6**, 564.

[15] D. J. A. de Waal and W. Robb, *Internat. J. Chem. Kinetics*, 1974, **6**, 309, 323.

[16] R. Roulet and R. Ernst, *Helv. Chim. Acta*, 1971, **54**, 2357.

[17] F. Basolo, J. C. Bailar, jun., and B. R. Tarr, *J. Amer. Chem. Soc.*, 1950, **72**, 2433.

constants were obtained from the gradients of these lines. Mean values from several determinations of $k_{obs.,1}$ are listed in Table 1. At a given pH, plots of $k_{obs.}$ against $[pd]_T$ were linear [equation (3)] where $[pd]_T$ represents the total

$$k_{obs.,1} = k_{S,1} + k_{L,1}[pd]_T \qquad (3)$$

concentration of pd in all its protonated and unprotonated forms [equation (4)]. Least-squares analysis of equation (3)

$$[pd]_T = [pd] + [Hpd^+] + [H_2pd^{2+}] \qquad (4)$$

gave the values of $k_{S,1}$ and $k_{L,1}$ listed in Table 1. Within 95% confidence limits, the intercept $k_{S,1}$ is genuine even

and entropies were calculated and are listed in Table 3. The various reaction paths to which these data refer are discussed in the following section.

The second reaction was followed at 360 nm, an isosbestic point for the species $[PtCl_4]^{2-}$ and $[Pt(pd)Cl_2]$ involved in the first reaction. At this wavelength an induction period was observed, the early stages of plots of $\log(A_t - A_\infty)$ against time being almost horizontal. As the reaction proceeded, however, $\log(A_t - A_\infty)$ decreased with time and the curve became linear, resembling in its latter stages an ordinary first-order plot. Values of the pseudo-first-order rate constant for the second reaction, $k_{obs.,2}$, were

TABLE 1

Ligand, hydrogen-ion, and temperature dependence of the reaction of $[PtCl_4]^{2-}$ with pd: first reaction, $[PtCl_4^{2-}] = 2.5 \times 10^{-3}$ mol dm$^{-3}$ and $I = 2.0$ mol dm$^{-3}$ (Na[ClO$_4$])

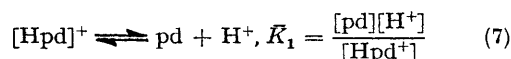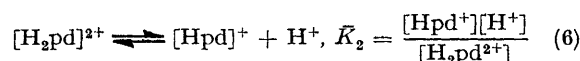| | | | | | $10^4 k_{obs.,1}/s^{-1}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 8.10 | 8.52 | 8.86 | 9.15 | 9.70 | 10.15 | 10.42 [a] | 11.00 | 9.70 | 9.70 | 10.42 | 10.42 |
| $T$/K | 298.2 | 298.2 | 298.2 | 298.2 | 298.2 | 298.2 | 298.2 | 298.2 | 305.5 | 311.5 | 305.5 | 311.5 |
| $[pd]_T$/mol dm$^{-3}$ | | | | | | | | | | | | |
| 0.25 | 0.42 | 0.86 | 1.35 | 2.02 | 2.55 | 3.15 | 3.49 | 3.52 | 5.07 | 8.43 | 7.17 | 10.70 |
| 0.20 | 0.33 | 0.71 | 1.05 | 1.65 | 2.09 | 2.57 | 2.78 | 2.72 | 4.39 | 6.65 | 5.85 | 8.97 |
| 0.15 | 0.30 | 0.60 | 0.84 | 1.38 | 1.61 | 2.01 | 2.28 | 2.33 | 3.21 | 5.45 | 4.84 | 7.68 |
| 0.10 | 0.26 | 0.45 | 0.61 | 1.09 | 1.18 | 1.39 | 1.73 | 1.54 | 2.42 | 3.95 | 3.32 | 5.08 |
| 0.05 | | 0.34 | 0.42 | 0.68 | 0.75 | 0.85 | 1.03 | | 1.49 | 2.49 | | |
| $k_{L,1}$/dm$^3$ mol$^{-1}$ s$^{-1}$ | 1.01 | 2.62 | 4.20 | 6.47 | 9.02 | 11.55 | 12.36 | 12.61 | 18.26 | 28.72 | 25.15 | 36.31 |
| 95% confidence limit | ±0.20 | ±0.29 | ±0.56 | ±0.63 | ±0.64 | ±0.74 | ±1.02 | ±1.19 | ±1.47 | ±2.47 | ±2.41 | ±3.16 |
| $k_{S,1}$ [b]/s$^{-1}$ | 0.15 | 0.20 | 0.20 | 0.39 | 0.28 | 0.26 | 0.48 | 0.32 | 0.56 | 1.09 | 0.89 | 1.75 |
| 95% confidence limit | ±0.05 | ±0.05 | ±0.09 | ±0.10 | ±0.11 | ±0.12 | ±0.18 | ±0.20 | ±0.24 | ±0.41 | ±0.42 | ±0.73 |

[a] $[pd]$ = 0.241, 0.193, 0.145, 0.096, and 0.048 mol dm$^{-3}$ respectively. [b] Average values: 0.29 (298.2), 0.73 (305.5), and 1.42 s$^{-1}$ (311.5 K).

though the 95% confidence limit is as large in some cases as half the value of the intercept. Despite the large scatter and confidence limits for the value of $k_{S,1}$ at constant temperature, there appears to be no systematic variation of $k_{S,1}$ with pH, and it is probably valid to conclude that $k_{S,1}$ is independent of hydrogen-ion concentration.

The value of $k_{L,1}$ increased with increasing pH and obeys relation (5), where $\bar{K}_1$ and $\bar{K}_2$ are the ionisation constants of

$$k_{L,1} = \frac{k_1 \bar{K}_1 \bar{K}_2 + k_1' \bar{K}_2[H^+]}{\bar{K}_1 \bar{K}_2 + \bar{K}_2[H^+] + [H^+]^2} \qquad (5)$$

the protonated forms of pd, defined by equations (6) and (7).

$$[H_2pd]^{2+} \rightleftharpoons [Hpd]^+ + H^+, \quad \bar{K}_2 = \frac{[Hpd^+][H^+]}{[H_2pd^{2+}]} \qquad (6)$$

$$[Hpd]^+ \rightleftharpoons pd + H^+, \quad \bar{K}_1 = \frac{[pd][H^+]}{[Hpd^+]} \qquad (7)$$

The values of $\bar{K}_1$ and $\bar{K}_2$ at $I = 2.0$ mol dm$^{-3}$ and 25 °C of Nasanen et al.[18-20] were checked experimentally and excellent agreement was obtained. For other temperatures, the values of $\bar{K}_1$ and $\bar{K}_2$ were determined by pH titration (Table 2). Plots of $k_{L,1}(\bar{K}_1\bar{K}_2 + \bar{K}_2[H^+] + [H^+]^2)$ against $[H^+]$ were linear and values of $k_1$ and $k_1'$ were extracted from the intercept and gradient, respectively, and are listed in Table 3. The gradients of the plots were extremely steep with the consequence that, although $k_1'$ could be determined with reasonable accuracy, the value of $k_1$ was subject to considerable error. From the temperature dependence of $k_1$ and $k_1'$, the activation enthalpies

obtained from the gradients of the linear portions of these curves. Mean values of $k_{obs.,2}$ thus obtained are listed in Table 4.

TABLE 2

Values of the acidity constants for propane-1,3-diamine [a]

| $T$/K | $pK_1$ | $pK_2$ |
|---|---|---|
| 298.2 [b] | 11.11 | 9.47 |
| 298.2 | 11.01 | 9.42 |
| 305.2 | 10.40 | 9.05 |
| 311.5 | 10.06 | 8.45 |

[a] Values quoted here are for the reactions $H^+ + H_{n-1}L \rightleftharpoons H_nL$ where $K_n = [H_nL]/[H^+][H_{n-1}L]$ in keeping with the usage in tables of stability constants ('Stability Constants of Metal-Ion Complexes,' Special Publ. Nos. 17 and 25, the Chemical Society, London, 1964 and 1971). $\bar{K}$, used for convenience in the text, is the reciprocal of $K$. [b] From refs. 17—19.

TABLE 3

Rate constants and activation parameters for the reaction of $[PtCl_4]^{2-}$ with pd

| $T$/K | $10^3 k_1$ | $10^3 k_1'$ | $10^3 k_2$ | $10^3 k_2'$ |
|---|---|---|---|---|
| | | dm$^3$ mol$^{-1}$ s$^{-1}$ | | |
| 298.2 | 2.4 ± 0.6 | 1.5$_3$ ± 0.15 | 2.0 ± 0.5 | 0.9$_3$ ± 0.1 |
| 305.5 | 3.1 ± 0.7 | 2.0$_4$ ± 0.20 | | |
| 311.5 | 4.1 ± 0.8 | 2.4$_8$ ± 0.20 | | |
| $\Delta H^{\ddagger}$/kJ mol$^{-1}$ | 32 ± 5 | 26 ± 3 | | |
| $\Delta S^{\ddagger}$/J K$^{-1}$ mol$^{-1}$ | −188 ± 30 | −210 ± 20 | | |

For the second reaction, statistical treatment of the rate constants showed that rate equation (8) is obeyed. No

$$k_{obs.,2} = k_{L,2}[pd]_T \qquad (8)$$

[18] R. Nasanen, M. Koskinen, R. Salonen, and A. Kiiski, Soumen Kem., 1965, B38, 81.
[19] R. Nasanen, M. Koskinen, and K. Kajander, Soumen Kem., 1965, B38, 103.
[20] R. Nasanen and M. Koskinen, Soumen Kem., 1967, B40, 23, 108.

evidence was found for a term independent of ligand concentration. The dependence of the rate constant $k_{L,2}$ on hydrogen-ion concentration, given by (9), is similar to

### TABLE 4

Ligand and hydrogen-ion dependence of the reaction of $[PtCl_4]^{2-}$ with pd: second reaction, $[PtCl_4{}^{2-}] = 2.5 \times 10^{-3}$ mol dm$^{-3}$, $[Cl^-] = 1.0$ mol dm$^{-3}$, $I = 2.0$ mol dm$^{-3}$ $(Na[ClO_4])$, 298.2 K

| | $10^4 k_{obs.,2}/s^{-1}$ | | | | |
|---|---|---|---|---|---|
| pH | 8.86 | 9.15 | 9.70 | 10.15 | 10.42* |
| [pd]/mol dm$^{-3}$ | | | | | |
| 0.25 | 0.77 | 0.88 | | 1.82 | 2.37 |
| 0.20 | 0.62 | 0.77 | 0.94 | 1.48 | 1.79 |
| 0.15 | 0.43 | 0.54 | 0.77 | 0.94 | 1.56 |
| 0.10 | 0.33 | 0.31 | 0.46 | 0.45 | 0.94 |
| 0.05 | 0.16 | 0.16 | 0.20 | 0.22 | 0.51 |
| $k_{L,2}$/dm$^3$ mol$^{-1}$ s$^{-1}$ | 3.03 | 3.80 | 5.05 | 8.47 | 9.47 |
| 95% confidence limit | $\pm 0.41$ | $\pm 0.41$ | $\pm 0.61$ | $\pm 0.91$ | $\pm 0.91$ |

\* [pd] = 0.241, 0.193, 0.145, 0.96, and 0.048 mol dm$^{-3}$, respectively.

that of $k_{L,1}$. Values of $k_2$ and $k_2'$, determined as above for reactions at 298.2 K, are listed in Table 3. The experi-

$$k_{L,2} = \frac{k_2 \bar{K}_1 \bar{K}_2 + k_2' \bar{K}_2 [H^+]}{\bar{K}_1 \bar{K}_2 + \bar{K}_2 [H^+] + [H^+]^2} \quad (9)$$

mental uncertainty in the values of $k_{L,2}$ is considerably greater than those for $k_{L,1}$, possibly because of the smaller optical-density changes at 360 nm, and because of the necessity to ensure that the induction period had been passed in the plot of $\log(A_t - A_\infty)$ against time. Consequently, the determination of the values of $k_2'$ and, in particular, $k_2$ is subject to considerable error. For these reaction paths, the inherent uncertainty of the values obtained did not justify attempts to obtain activation parameters, and temperature-dependence studies were not made.

### DISCUSSION

The reaction $[PtCl_4]^{2-} + pd \longrightarrow [Pt(pd)Cl_2] + 2Cl^-$ involves two steps, replacement of a chloride ligand by one end of the bidentate amine, followed by closure of the chelate ring. The same two processes are involved in the formation of $[Pt(pd)_2]^{2+}$ from $[Pt(pd)Cl_2]$. Ring closure has always been tacitly assumed to be rapid compared with the initial step, and this has been verified by Carter and Beattie [21] for the closure of en rings. Therefore, the two reaction rates measured above correspond to the rates of formation of the first Pt–N bond of each chelate ring.

The rate constant $k_{obs.,1}$ for the first reaction contains
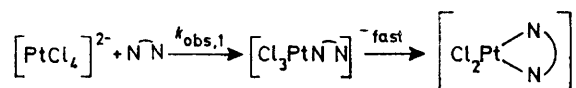


a term, $k_{S,1}$, independent of the ligand concentration. In square-planar systems such a term is usually attributed to rate-determining formation of a highly reactive solvated complex which in turn rapidly reacts with the incoming ligand. In the present system, $[PtCl_4]^{2-}$ is

equilibrated in aqueous sodium chloride–sodium perchlorate (pH 4—5) containing sufficient chloride to ensure that the only species present in significant concentration [22] are $[PtCl_4]^{2-}$ and $[PtCl_3(OH_2)]^-$. When this equilibrated solution is mixed with solutions of pd, the pH rises essentially to that of the pd solution which acts as its own buffering system. The aqua-complex is sufficiently acidic [23] that deprotonation (10) is extensive at the lower end of the pH range studied and essentially complete at the higher values. From the value of

$$[PtCl_3(OH_2)]^- \rightleftharpoons [PtCl_3(OH)]^{2-} + H^+,$$
$$pK_a \ ca. \ 7 \quad (10)$$
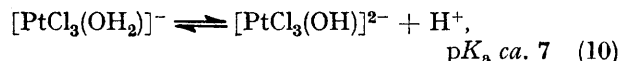
Grantham et al.[23] of 0.018 mol dm$^{-3}$ for the equilibrium constant of (2) and the acidity constant above, the equilibrium constant for (11) can be calculated [8] to be ca. $10^5$ mol dm$^{-3}$.

$$[PtCl_4]^{2-} + OH^- \rightleftharpoons [PtCl_3(OH)]^{2-} + Cl^- \quad (11)$$
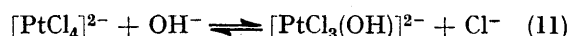
However, since hydroxo-complexes are obtained by deprotonation of aqua-complexes rather than by direct substitution,[24] the rate of formation of the hydroxo-complex will equal the rate of formation of the aqua-complex. Therefore, equilibrated solutions will differ from fresh solutions of $[PtCl_4]^{2-}$ only in the concentration of $[PtCl_3(OH)]^{2-}$ initially present after admixture of the ligand. If the hydroxo-complex is mechanistically important, a correlation should be observed between its concentration and the observed rate. As can be seen in Table 5, fresh solutions initially containing effectively

### TABLE 5

Chloride dependence of the reaction of $[PtCl_4]^{2-}$ with pd. $[PtCl_4{}^{2-}] = 2.5 \times 10^{-3}$ mol dm$^{-3}$, [pd] = 0.25 mol dm$^{-3}$, pH 8.91, $I = 2.0$ mol dm$^{-3}$ $(Na[ClO_4])$, 298.2 K

| $[Cl^-]$ mol dm$^{-3}$ | $\dfrac{100[PtCl_3(OH_2)^-]}{[PtCl_4{}^{2-}]}$ | First reaction $10^4 k_{obs.,1}/s^{-1}$ | Second reaction $10^4 k_{obs.,2}/s^{-1}$ |
|---|---|---|---|
| 1.00 | 1.30 | 2.12 | 1.04 |
| 0.75 | 1.73 | 2.12 | 1.06 |
| 0.50 | 2.60 | 2.05 | 1.09 |
| 0.30 | 4.33 | 2.07 | 1.07 |
| 0.15 | 8.66 | 1.94 | 1.11 |
| 0.05 | 26.00 | 1.94 | 1.08 |
| 0.0 * | | 2.02 | 1.09 |
| Mean | | $2.04 \pm 0.10$ | $1.08 \pm 0.04$ |

\* Freshly prepared solution not in hydrolytic equilibrium.

no hydroxo-complex and solutions containing up to 26% of the total platinum as $[PtCl_3(OH)]^{2-}$ react at the same rate. The reason for this apparent contradiction seems to lie in the statistical limitations on the detection of such an effect. The ligand-independent path constitutes a small part of the total observed rate (Table 1), and the inherent error in the measurement of $k_{S,1}$ is sufficiently large as to render apparent variations meaningless. The mean value of $k_{S,1}$ is in very good agreement with the rate constant $(0.4 \times 10^{-4}$ s$^{-1})$ of Grantham et al.[23] for the hydrolysis of $[PtCl_4]^{2-}$. This

[21] M. J. Carter and J. K. Beattie, *Inorg. Chem.*, 1970, **9**, 1233.
[22] L. I. Elding, *Acta Chem. Scand.*, 1970, **24**, 1527.
[23] L. F. Grantham, T. S. Elleman, and D. S. Martin, jun., *J. Amer. Chem. Soc.*, 1955, **77**, 2965.
[24] D. Banerjea, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1957, **79**, 4055.

suggests that the reaction path described by $k_{S,1}$ involves rate-determining formation of $[PtCl_3(OH_2)]^-$ followed by fast reaction of one or both of the pd species discussed below with $[PtCl_3(OH)]^{2-}$. It is interesting to compare this finding with those of Teggins et al.[7,8] for the reactions of dien with $[PtCl_4]^{2-}$ and $[PtBr_4]^{2-}$, where no ligand-independent path was observed at all. It is unlikely that the reason for the non-observance of the solvent path was its small contribution to the overall rates, since these were of the same order of magnitude as those discussed in the present paper. It is difficult to suggest a reason for the non-participation of the solvent path in the dien reactions, but similar anomalies have been observed in other platinum(II) systems.[25,26] Further studies on related systems are indicated.

The ligand-dependent term $k_{L,1}$ in the rate law for the formation of $[Pt(pd)Cl_2]$ shows a complicated hydrogen-ion dependence, which can be interpreted as follows. The ligand species present in solution are the unprotonated form pd, and the mono- and di-protonated
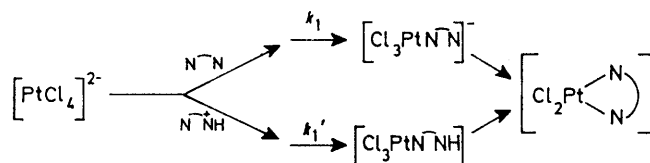


forms $[Hpd]^+$ and $[H_2pd]^{2+}$, respectively. The latter form can be expected to be unreactive in accord with the findings of Teggins et al.[7,8] that the fully protonated form of dien does not function as a ligand. Equilibria (6) and (7) obtain in the reaction mixture. Rate-determining attack of pd and $[Hpd]^+$ on $[PtCl_4]^{2-}$ followed by ring closure, accompanied by deprotonation of the free amine nitrogen in the latter case, yields rate law (12). The ligand-dependent term $k_{L,1}$ in (3) would

$$-d[PtCl_4]^{2-}/dt = (k_1[pd] + k_1'[Hpd^+])[PtCl_4]^{2-} \quad (12)$$

thus be equal to $k_1[pd] + k_1'[Hpd^+]$ and direct substitution of (6) and (7) into (12) yields the experimental rate equation (5).

The ligand-dependent term thus represents parallel attack of two species of ligand on the same platinum substrate. It is instructive to compare the present results with those obtained by Robb and his co-workers[13-15] for the reactions of ethylenediamine with $[PdCl_4]^{2-}$ and $[AuCl_4]^-$. The reactions of palladium(II) and gold(III) complexes are faster, often by factors of $10^2$—$10^4$, than the corresponding platinum(II) species.[6] In order to reduce the rates of formation of the palladium and gold complexes of en to measurable speeds, the reactions were conducted in acidic solutions in which the unprotonated form of the ligand was totally absent, and only an equilibrium of the type (6) needed to be considered. However, the hydrolyses of both $[PdCl_4]^{2-}$ and $[AuCl_4]^-$ are fast equilibria under these conditions

and $[AuCl_3(OH_2)]$ is considerably more acidic than $[PtCl_3(OH_2)]^-$. Only ligand-dependent paths were obtained and the dependence of the observed rate constants on hydrogen- and chloride-ion concentrations showed that the species participating in the second-order rate-determining steps with the monoprotonated form of the ligand $[Hen]^+$, were $[PdCl_4]^{2-}$ and $[PdCl_3(OH_2)]^-$ in the palladium case, and $[AuCl_4]^-$ and $[AuCl_3(OH)]^-$ in the gold system.

The involvement of aqua- or hydroxo-species in these reaction systems resembles the behaviour found by Rund and his co-workers[1,2,4] for the reaction of $[PtCl_4]^{2-}$ with phen, in that the formation of the solvated species is fast by comparison with the substitution reaction. Complexes of platinum are considerably more inert than those of palladium or gold, so that the rate of solvolysis is an important aspect of the kinetics of its substitution reactions. Only for highly unreactive ligands, such as bipy or phen, can the solvolysis be treated as a fast pre-equilibrium. Rund suggested that the low reactivity of phen and bipy derives from the steric rigidity of their structure. The kinetics observed in the present study, although in accordance with that conclusion, do not constitute supporting evidence. However, the observed rate laws do provide quantitative data for a flexible bidentate ligand which may serve as a basis with which to compare other ligand systems.

The activation parameters for the $k_1$ and $k_1'$ paths are of interest in that $\Delta H^{\ddagger}$ values are very low, but $\Delta S^{\ddagger}$ values are high and negative. Negative entropies of activation are characteristic of associative mechanisms, and could well be as high as they are because of stringent steric requirements in the transition state.[27] This is expected in cases where only certain directions of approach of the ligand to the complex facilitate reaction.[28] Baracco et al.[10] measured activation parameters for the reaction of $[PtCl_2(bipy)]$ with a number of diamines in methanol or methanol–water mixtures. The observed activation parameters are solvent dependent which is expected, not least because of the conjugate base relation between the base and water. Reactions of half-neutralised solutions of en were assumed to give the kinetic behaviour of $[Hen]^+$. However, this paper shows that, without a full consideration of the pH dependence, the competing paths of en and $[Hen]^+$ cannot be separated. Interestingly, the effective activation energy determined from the temperature dependence of $k_{L,1}$ (67 kJ mol$^{-1}$) is approximately equal to the sum of the activation energies of the two paths $k_1$ and $k_1'$ (34 + 29 = 63 kJ mol$^{-1}$), and is also similar to the values of 75 and 73 kJ mol$^{-1}$ found by Kukushkin and Ukraintsev[11] for the reactions of $[PtCl_4]^{2-}$ with en and pn, respectively. These workers, too, did not investigate the pH dependence of the reaction, nor did they investigate the possibility of a ligand-independent

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path, so that it is likely that their values contain a contribution from this term as well.

For the second reaction, $[Pt(pd)Cl_2] + pd \longrightarrow [Pt(pd)_2]^{2+} + 2Cl^-$, the observed rate law has no term independent of ligand concentration. The rate of acid hydrolysis of the related complex $[Pt(en)Cl_2]$ has

$k_{L,2}$, shows exactly the same hydrogen-ion dependence as $k_{L,1}$, suggesting that similar mechanistic steps operate. The rate-determining reaction is also schematically similar to the reaction of $[Pt(en)Cl_2]$ with ammonia, and enables a comparison to be made between reaction of chemically related uni- and bi-dentate
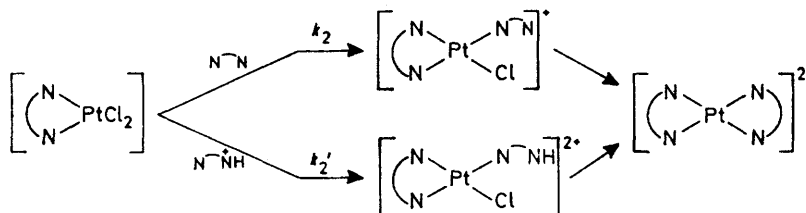


been reported [29] to be $0.49 \times 10^{-4}$ s$^{-1}$. Making the reasonable assumption that a similar value should hold for $[Pt(pd)Cl_2]$, it can be seen from Table 3 that reaction of $[Pt(pd)Cl_2]$ with pd *via* this hydrolysis step should constitute an appreciable fraction of the observed rate. Non-observance of the solvent path here cannot be attributed to experimental or statistical factors, although the reason for this deviation from ' classical ' square-planar kinetic behaviour is not clear.

The rate constant for the ligand-dependent path,

entering groups. The values of $k_2$ and $k_2'$ (Table 3) are greater than those found by Belluco *et al.*[30] for the reaction of $[Pt(en)Cl_2]$ with $NH_3$ by factors of 2—4. Despite the limited meaning of this statement, since the pH dependence of the latter reaction was not investigated, the slightly greater reactivity of the bidentate ligand is in qualitative agreement with similar observations by Baracco *et al.*[10] and by Kukushkin and Ukraintsev.[11]

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