

The Stepwise Dissociation of the Tetrachloroplatinate(II) Ion in Aqueous Solution

V. Chloride Anations of the Chloro Aqua Complexes of Platinum(II)

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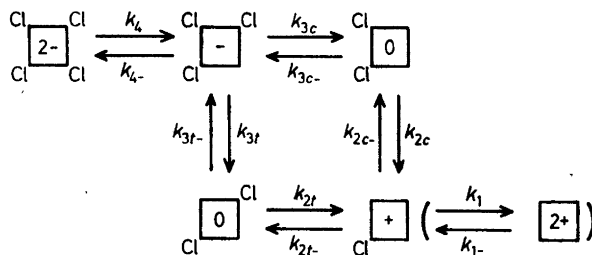
The chloride anations of $\text{PtCl}(\text{H}_2\text{O})_3^+$, *cis*- $\text{PtCl}_2(\text{H}_2\text{O})_2$, *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$, and $\text{PtCl}_3\text{H}_2\text{O}^-$ have been studied spectrophotometrically by adding excess chloride to dilute, aged solutions of K_2PtCl_4 . The reactions are first order with respect to chloride and complex. Rate constants at 15, 25, and 35°C are given in Table 5, activation enthalpies and entropies in Table 6. A reaction model for the stepwise substitutions of the chloride ligands of PtCl_4^{2-} by water and the reverse chloride anations of the aqua complexes, including *cis*- and *trans*-isomers of $\text{PtCl}_2(\text{H}_2\text{O})_2$, is given in Fig. 1. Ionic strength 0.500 M; medium HClO_4 .

Previous papers¹⁻⁴ on this subject have been concerned with the composition of equilibrated solutions of K_2PtCl_4 and with the kinetics of the acid hydrolysis^{5,p.158} of PtCl_4^{2-} and of the chloride anation^{5,p.193} of $\text{PtCl}_3\text{H}_2\text{O}^-$. The present paper deals with the chloride anations of $\text{PtCl}(\text{H}_2\text{O})_3^+$, *cis*- $\text{PtCl}_2(\text{H}_2\text{O})_2$, *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ and $\text{PtCl}_3\text{H}_2\text{O}^-$. In a subsequent paper,⁶ an investigation of the equilibrium between the *cis*- and *trans*-isomers of $\text{PtCl}_2(\text{H}_2\text{O})_2$ and of the rates of formation of the aqua complexes in aging solutions of K_2PtCl_4 is reported.*

Fig. 1 shows a model which can be used to describe the experimental results. Each square represents a complex species $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$, $n = 1, 2, 3, 4$. Only the chloride ligands and the ionic charge of each species have been marked.** The acid hydrolyses are first order with respect to complex, having rate constants k_n , s^{-1} . The reverse chloride anations are first order with respect to both complex and chloride, the rate constants being k_{n-} , $\text{s}^{-1}\text{M}^{-1}$. The equilibrium constants for the substitution reactions, K_n , M, are also defined in

* A preliminary report on these investigations was given at the 10th International Conference on Coordination Chemistry in Tokyo, 1967.

** In the following text, the water ligands will also be excluded.



$$K_n = [\text{PtCl}_{n-1}(\text{H}_2\text{O})_{5-n}^{3-n}] \times [\text{Cl}^-] \times [\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}]^{-1}; \quad n = 1, 2, 3, 4.$$

$$K_{3r} = [\text{trans-PtCl}_2(\text{H}_2\text{O})_2] \times [\text{Cl}^-] \times [\text{PtCl}_3\text{H}_2\text{O}^-]^{-1}; \quad K_{3c} = K_3 - K_{3r}$$

$$K_{2r} = [\text{PtCl}(\text{H}_2\text{O})_3] \times [\text{Cl}^-] \times [\text{trans-PtCl}_2(\text{H}_2\text{O})_2]^{-1}; \quad K_{2c}^{-1} = K_2^{-1} - K_{2r}^{-1}$$

Fig. 1. Reaction scheme for the stepwise substitution of the chloride ligands of PtCl_4^{2-} by water. The water ligands have been omitted. The acid hydrolyses are first order with respect to complex, the chloride anions are first order with respect to both complex and chloride.

the figure. The reactions marked by vertical arrows are, with the exception of that described by the rate constant k_{2c-} , slower than those marked by horizontal arrows by a factor of at least 100.

The reaction scheme includes two geometrical isomers of the neutral complex. According to the *trans*-effect (Chernyajev⁷), the acid hydrolysis of PtCl_3^- would be expected to give primary *cis*- PtCl_2 , since the *trans*-effect of chloride is greater than that of water,^{8,p.24} and therefore a *cis*-isomer would be formed much faster than a *trans*-isomer. Experimental studies of the acid hydrolysis of PtCl_3^- , which will be described in a subsequent paper,⁶ and of the chloride anation of PtCl_2 , indicate the occurrence of a *trans*-isomer also.

The latter reaction may be studied by adding chloride in excess to a solution containing the complex PtCl_2 almost exclusively. Such a solution (only

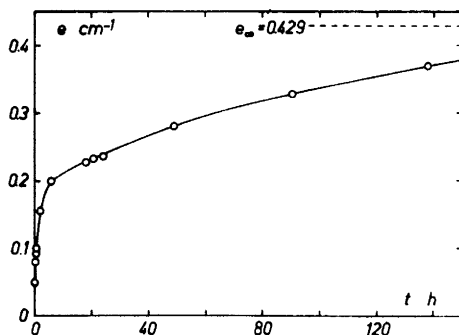
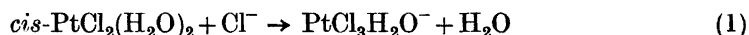


Fig. 2. Change of absorptivity at 230 nm with time for a solution containing, at zero time, $\text{PtCl}_2(\text{H}_2\text{O})_2$ (6.33×10^{-5} M) and chloride (0.0500 M). The solution was obtained by percolating a solution of K_2PtCl_4 (5×10^{-3} M) containing HClO_4 (0.5 M), which had been aged for 8 months, through an anion exchange column in perchlorate form and adding 0.500 M HCl to the eluate.

negligible amounts of cationic species will be present) may be prepared by percolating an aged solution of K_2PtCl_4 through a perchlorate saturated anion exchange column (details in Ref. 1). The change of absorptivity with time, shown in Fig. 2, indicates the occurrence of one fast and one slow reaction. Using the reaction model of Fig. 1, the fast increase of absorptivity, observed during the first 5 h, is due to the reaction



and a consecutive, slower, chloride anation of PtCl_3^- . The slow change, observed thereafter for a period of several days, is caused by the reaction



followed by the much faster chloride anation of PtCl_3^- .

Instead of this suggested model, one of the two neutral species observed, most likely the slow reacting one, might be thought to be a polynuclear complex, forming slowly in aging solutions of K_2PtCl_4 and breaking up again slowly, when chloride is added. This possibility, however, is disproved by other experiments (*cf.* p. 1351 and Ref. 6).

To study reactions (1) and (2), it will not be necessary to use solutions containing PtCl_2 exclusively, prepared by means of anion exchangers. The reactions may be followed simply by adding chloride in excess to aged, dilute solutions of K_2PtCl_4 , containing a mixture of the different complexes. The rate constants calculated remain the same.

The reactions studied are reversible. Thus, the species PtCl_3^- , $cis\text{-PtCl}_2$, $trans\text{-PtCl}_2$ and PtCl^+ , formed by the consecutive acid hydrolysis reactions, can be quantitatively recovered as PtCl_4^{2-} by adding excess chloride. This is shown by the reappearance of the typical spectrum of PtCl_4^{2-} . The acid solutions used are stable, or, more correctly, metastable (*cf.* Ginstrup and Leden ^{9,p.2694}) against oxidation by air and against disproportionation.

CHLORIDE ANATION OF $cis\text{-PtCl}_2(\text{H}_2\text{O})_2$

The anation reaction (1) was followed at 210 and 287 nm by adding chloride to aged solutions of K_2PtCl_4 . At the wavelengths used, the molar absorptivities of PtCl_4^{2-} , ϵ_4 , and of PtCl_3^- , ϵ_3 , are equal (Ref. 2, Fig. 1). Thus, the observed change of absorbance will be due to reaction (1) exclusively, while the simultaneous and slower chloride anation of PtCl_3^- will cause no change.

By aging the solutions of K_2PtCl_4 for short periods, only very small concentrations of $trans\text{-PtCl}_2$ will be formed.⁶ The reverse reaction (*i.e.* the acid hydrolysis of PtCl_3^-) was suppressed by choosing the concentration of chloride ions greater than about 2×10^{-2} M at the kinetic runs. Then less than 2 % of the platinum will be left as PtCl_2 at the final equilibrium (Ref. 1, Fig. 5).

If the concentration of platinum, C_{Pt} M, is much smaller than that of chloride, b M, a simple reaction of first order is obtained. At 210 nm, the molar absorptivities are high ($\epsilon_4 = \epsilon_3 = 7600$; $\epsilon_2 = 3200$) and this condition is easy to fulfil. At 287 nm, on the other hand, the molar absorptivities are so small ($\epsilon_4 = \epsilon_3 = 26$; $\epsilon_2 = 63$) that C_{Pt} has to be at least about 4×10^{-3} M to give

measurable absorbances. Solutions of K_2PtCl_4 having this concentration of platinum, however, will contain only about 10 % of *cis*- $PtCl_2$ at equilibrium. This will give too small a change of absorptivity to permit accurate calculations.

Colvin¹⁰ has shown that solutions of K_2PtCl_4 made alkaline by adding hydroxide (to 0.1 M) and aged for 1 to 2 days will contain mainly the complex $PtCl_2(OH)_2^{2-}$. The kinetic experiments reported here indicate that this is the *cis*-isomer. By adding perchloric acid to such solutions, the aquocomplex *cis*- $PtCl_2(H_2O)_2$ is formed and reaction (1) may be followed also at 287 nm as described above.

Experimental

Chemicals and apparatus were the same as in Refs. 2 and 3.

Measurements at 210 nm. Solutions of K_2PtCl_4 (10^{-4} – 3×10^{-4} M) in $HClO_4$ (0.500 M), containing no extra chloride, were aged for 12 to 20 h at 15, 25, or 35°C. Within this time, the equilibria between $PtCl_4^{2-}$, $PtCl_3^-$ and *cis*- $PtCl_2$ are almost established. Since the half-life of the formation of *trans*- $PtCl_2$ is about 270 h at 25°C (Ref. 6), only negligible amounts of this complex will be formed. Stock solutions made by mixing 0.500 M HCl and 0.500 M $HClO_4$ and having the following concentrations of chloride: 0.02000, 0.0400, 0.1000, 0.1500, and 0.2000 M, were also thermostated.

Slow kinetic runs with half-lives greater than about 3 min were started by mixing equal volumes of platinum solution and chloride solution in flasks, kept in thermostats at the desired temperature $\pm 0.02^\circ C$. Samples were withdrawn with thermostated pipettes at time intervals and the absorbance measured in 1 or 0.5 cm cells. Kinetic runs having half-lives less than 3 min were started by mixing the solutions directly in the thermostated 1 cm cells, using thermostated syringes (1.500 ml). No influence of light on the rate of reaction was observed.

Measurements at 287 nm. Solutions of K_2PtCl_4 (about 4×10^{-3} M) containing KOH (0.020 M) were aged for about 12 h at 25°C. The chloride stock solutions were made by mixing 1.000 M HCl and 1.000 M $HClO_4$. They had the following concentrations of chloride: 0.1000, 0.2000 and 0.400 M. 2.500 ml of each solution were mixed using thermostated syringes in a 4 cm thermostated cell and the change of absorbance was followed *vs.* time at $25.0 \pm 0.1^\circ C$. Some heat (about 0.6 cal) is evolved when the solutions are mixed because of neutralisation of the hydroxide. This will cause a rise of temperature less than $0.1^\circ C$, which may be neglected.

Results

The rate of reaction (1) is simply

$$-d[cis-PtCl_2]/dt = k_{exp}[cis-PtCl_2] \quad (3)$$

where $k_{exp} = k_{3c-} \cdot b$. Integrating and introducing absorptivities instead of concentrations gives

$$k_{exp} \cdot t = \ln(e_0 - e_\infty)/(e - e_\infty) \quad (4)$$

In Fig. 3, some examples of logarithmic plots at different *b*'s are given. The values of k_{exp} obtained from the slope of such plots are given in Table 1. Plots of k_{exp} *vs.* *b* give straight lines passing through the origin (Fig. 4). The reaction is thus first order with respect to chloride. The obtained values of k_{3c-} at the three temperatures are given in Table 5.

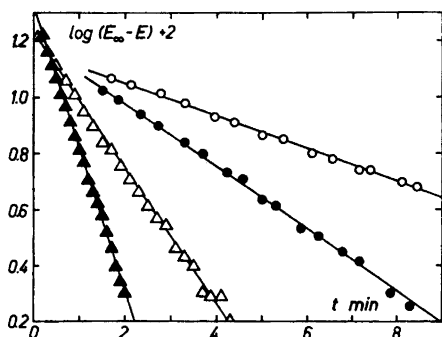


Fig. 3. Chloride anation of *cis*-PtCl₂(H₂O)₂. Plots of $\log(E_{\infty} - E)$ as a function of time; 35°C, 210 nm. The concentration of chloride was (from above) 10.0, 20.0, 50.0, and 100.0 mM. The total concentration of platinum was 0.288, 0.288, 0.144, and 0.150 mM. The cell thickness was 0.501 (O, ●) and 1.000 (Δ, ▲) cm.

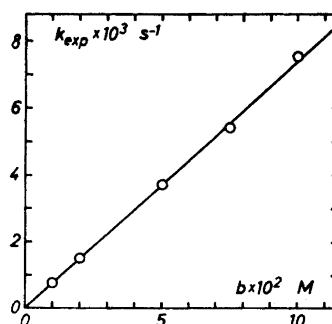


Fig. 4. Chloride anation of *cis*-PtCl₂(H₂O)₂. The rate constant $k_{\text{exp}} = k_{3c-} \cdot b$ (s⁻¹) of eqn. (3) as a function of the concentration of chloride, b M; 25°C, 210 nm.

Table 1. Chloride anation of *cis*-PtCl₂(H₂O)₂. The rate constant $k_{\text{exp}} = k_{3c-} \cdot b$ (s⁻¹) of eqn. (3) at 15, 25, and 35°C. The concentration of chloride is b M. Measurements at 210 nm. The error in k_{exp} , estimated from the graphs, is about 3 %.

| $b \times 10^3$ | $k_{\text{exp}} \times 10^3$ | | |
|-----------------|------------------------------|------|------|
| | 15°C | 25°C | 35°C |
| 10.0 | 0.267 | 0.77 | 2.20 |
| 20.0 | 0.54 | 1.51 | 4.2 |
| 50.0 | 1.23 | 3.7 | 9.7 |
| 75.0 | 1.96 | 5.4 | 15.2 |
| 100.0 | 2.51 | 7.5 | 19.8 |

In Fig. 5 the experiments at 287 nm and 25°C, using alkaline solutions of K₂PtCl₄ to prepare *cis*-PtCl₂, have been plotted. From the slope of the line the rate constant $k_{3c-} = (7.5 \pm 0.2) \times 10^{-2}$ (s⁻¹M⁻¹) is obtained, *i.e.* a value in close agreement with that obtained from the measurements at 210 nm given in Table 5.

The total concentration of platinum was varied between 5×10^{-5} and 1.5×10^{-4} M in the experiments at 210 nm, and was about 2×10^{-3} M in the experiments at 287 nm. The exact concentration of *cis*-PtCl₂ in the different experiments was unknown, but varied in the same manner, *i.e.* by a factor of about 40. Since the rate constants obtained remain the same in this interval of concentration, reaction (1) is first order with respect to complex also.

The temperature dependence of the rate constant k_{3c-} shown in Fig. 6 gave the activation enthalpies and entropies of Table 6.

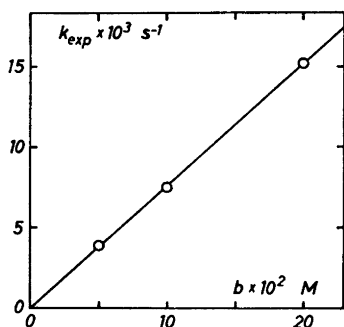


Fig. 5. Chloride anation of *cis*-PtCl₂(H₂O)₂. Experiments at 287 nm. The rate constant $k_{\text{exp}} = k_{3c-} \cdot b$ (s⁻¹) as a function of the concentration of chloride, b M; 25°C.

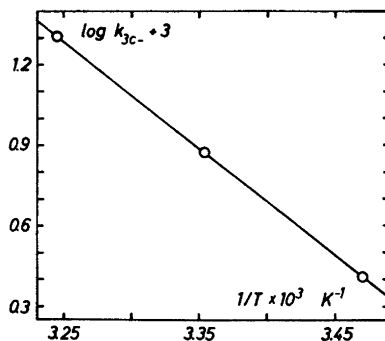


Fig. 6. Chloride anation of *cis*-PtCl₂(H₂O)₂. Temperature dependence of the rate constant k_{3c-} .

The PtCl₂(OH)₂²⁻ formed in alkaline solutions of K₂PtCl₄ seems to be the *cis*-isomer almost exclusively, if the aging is not prolonged more than 1 to 2 days. This can be shown by adding hydrochloric acid in excess to alkaline solutions, and following the change of absorbance *vs.* time at 230 nm as described in Fig. 2. In such experiments, no slow-reacting species having the typical half-life of *trans*-PtCl₂, can be discovered.

If, on the other hand, the aging of alkaline solutions is prolonged for more than 1 to 2 days at 25°C an increasing part of the platinum cannot be recovered as PtCl₄²⁻ by adding HCl. The absorbance of such solutions increases continuously in the UV, and old solutions show Tyndall effect. Thus it is obvious that if the base hydrolysis^{5,p.158} continues to complexes containing less than two chloride ligands per platinum, or if *trans*-PtCl₂(OH)₂²⁻ is formed, slow, irreversible changes will occur, comprising the formation of polynuclear or even colloidal species.

CHLORIDE ANATION OF *trans*-PtCl₂(H₂O)₂

Experimental

Chemicals and apparatus were the same as in Refs. 2 and 3.

Measurements. Solutions of K₂PtCl₄ (4×10^{-4} – 1×10^{-3} M) without extra chloride, containing perchloric acid (0.500 M), were aged at 25 or 35°C. The time of aging varied between 2 days and 1 year. Sometimes the solutions were aged at 60°C instead, which speeds up the rate of formation of *trans*-PtCl₂ compared to that at 25°C by a factor of 30 to 40. These solutions were rethermostated at the temperature of measurement, 25.00 or 35.00 ± 0.02°C.

At the beginning of the investigation, the platinum solutions were percolated through anion exchange columns before the kinetic runs were started, as was described in the introduction, but this did not appear to be necessary. The major part of the experiments was carried out using aged solutions directly.

Stock solutions made by mixing 0.500 M HCl and 0.500 M HClO₄ had the following concentrations of chloride: 0.500, 0.400, 0.2000, 0.1000, 0.0500, and 0.0400 M. The kinetic runs were started by mixing these solutions with the aged solutions of K₂PtCl₄ in thermostated flasks. The increase of absorbance was measured at 230 nm.

The equilibrium values of absorbance, E_{∞} , were measured after about 7 half-lives. They agreed with the values calculated using the equilibrium constant K_4 and the molar absorptivities ϵ_4 and ϵ_3 determined earlier.¹⁻⁴

Results

The aged solutions used contain about 20–50 % of *trans*-PtCl₂ and also small amounts of the positively charged complex PtCl⁺ (cf. Ref. 4). These two species are in a relatively fast equilibrium with each other (*vide infra*). When chloride is added in excess most of the PtCl⁺ will react rapidly with chloride to form *trans*-PtCl₂ until its concentration satisfies eqn. (5)

$$[\text{PtCl}^+] = K_{2t} \cdot [\textit{trans}\text{-PtCl}_2] \cdot b^{-1} \quad (5)$$

Here, $[\text{PtCl}^+] \ll [\textit{trans}\text{-PtCl}_2]$, since K_{2t} is 2.2×10^{-4} (Ref. 6, Table 2) and $b > 0.02$ (M).

In the same manner, the distribution of platinum on the species PtCl₄²⁻, PtCl₃⁻, and *cis*-PtCl₂ will relatively quickly attain the equilibrium distribution defined by the concentration of chloride, b (at 25°C, the half-life is about 2 h when b is 0.02 M and about 15 min when b is 0.25 M).

The slow change observed when these rapid equilibria have been established, shown in Fig. 2, is due to the reaction with chloride of the equilibrium mixture of *trans*-PtCl₂ and PtCl⁺ to the equilibrium mixture of PtCl₄²⁻, PtCl₃⁻ and *cis*-PtCl₂ along the two paths marked by vertical arrows in Fig. 1.

The reverse reactions are suppressed, since the concentration of chloride ions is greater than about 0.02 M (Ref. 1, Fig. 5). Then, the rate of disappearance of the PtCl⁺–*trans*-PtCl₂ mixture is

$$-d[\textit{trans}\text{-PtCl}_2]/dt = k_{2c-} \cdot b \cdot [\text{PtCl}^+] + k_{3t-} \cdot b \cdot [\textit{trans}\text{-PtCl}_2] \quad (6)$$

The concentration of *trans*-PtCl₂ can be expressed as

$$[\textit{trans}\text{-PtCl}_2] = (e_{\infty} - e) / (\epsilon_{\text{eq}} - \epsilon_t) \quad (7)$$

where ϵ_{eq} and ϵ_t are the molar absorptivities of the equilibrium mixture of PtCl₄²⁻, PtCl₃⁻ and *cis*-PtCl₂ and of *trans*-PtCl₂ respectively, and e and e_{∞} are the absorptivities of the complex solution at time t and at equilibrium, respectively.

Integrating eqn. (6) after introducing eqns. (5) and (7) will give

$$\ln(e_{\infty} - e) = -k_{\text{exp}} \cdot t + \text{const.} \quad (8)$$

where

$$k_{\text{exp}} = k_{3t-} \cdot b + k_{2c-} \cdot K_{2t} \quad (9)$$

Fig. 7 shows some typical logarithmic plots at different b 's. The rate constant k_{exp} is obtained from the slope of such plots according to eqn. (8). Table 2 gives the values obtained at the two temperatures.

The rate of the reaction is independent of the concentration of hydrogen ions. Three kinetic runs, having the same concentration of chloride ions (0.250 M) and varying concentrations of hydrogen ions (0.500, 0.250, and 0.125 M), gave identical values of k_{exp} .

Fig. 7. Chloride anation of *trans*-PtCl₂(H₂O)₂. Plots of $\log(e_{\infty} - e)$ as a function of time at 35°C. The concentration of platinum was 9.02×10^{-5} M. The concentration of chloride was 25.05 (○), 50.1 (●), 100.2 (△), and 250.5 mM (▲). The lines were parallel displaced by adding a term *A* to the ordinates: 2.2 (○), 2.1 (●), 2.0 (△) and 1.9 (▲). Cell 1.000 cm. Wavelength 230 nm.

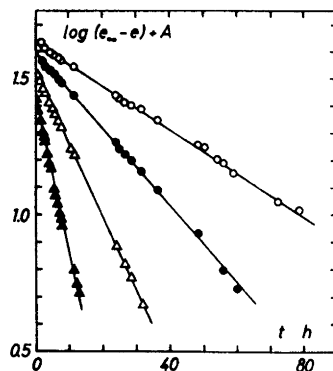


Table 2. Chloride anation of *trans*-PtCl₂(H₂O)₂. The rate constant k_{exp} s⁻¹ defined by eqn. (9) at 25 and 35°C. The concentration of chloride is *b* M. For the experiments at 25°C, C_{Pt} varied between about 6×10^{-5} and 1.2×10^{-4} (M), for those at 25°C, C_{Pt} was 9.02×10^{-5} in all experiments. The error in k_{exp} , estimated from the graphs, is about 4% at 25°C and 2% at 35°C.

| 25°C | | 35°C | |
|-----------------|------------------------------|-----------------|------------------------------|
| $b \times 10^3$ | $k_{\text{exp}} \times 10^6$ | $b \times 10^3$ | $k_{\text{exp}} \times 10^6$ |
| 20.00 | 1.04 | 25.05 | 5.0 |
| 50.0 | 2.62 | 50.1 | 9.0 |
| 100.0 | 4.7 | 100.2 | 17.2 |
| 200.0 | 9.7 | 200.5 | 33.4 |
| 250.0 | 11.6 | 250.5 | 43.1 |

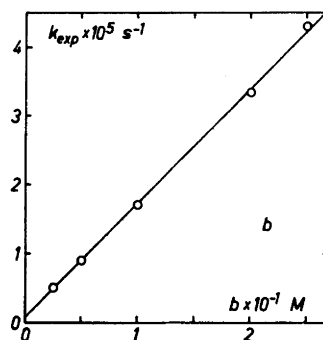
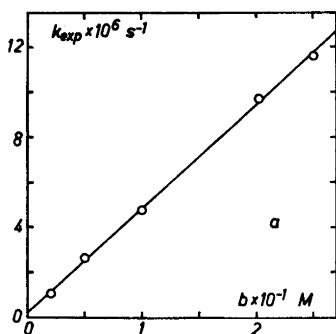


Fig. 8. Chloride anation of *trans*-PtCl₂(H₂O)₂. The rate constant k_{exp} s⁻¹ defined by eqn. (9) as a function of the concentration of chloride, *b* M, at 25°C (a) and at 35°C (b).

Plots of k_{exp} vs. b (Fig. 8 a, b) give straight lines having slope k_{3t-} and a small but definite ordinate axis intercept, $k_{2c-} \cdot K_{2t}$, according to eqn. (9). Reaction (2) is thus first order with respect to chloride. The concentration of platinum was varied also, showing that the reaction is first order with respect to complex (*vide* Table 2).

The ordinate axis intercept, $k_{2c-} \cdot K_{2t}$ can only be determined with an uncertainty of about 50 %. It was obtained as $(2 \pm 1) \times 10^{-7} \text{ s}^{-1}$ at 25°C and as $(8 \pm 4) \times 10^{-7} \text{ s}^{-1}$ at 35°C. The equilibrium constant K_{2t} is calculated in the subsequent paper ⁶ to be $2.2 \times 10^{-4} \text{ M}$ at 25°C and $2.4 \times 10^{-4} \text{ M}$ at 35°C. The error of this constant is about 25 %. Consequently, approximate values of k_{2c-} may be calculated from the intercepts. They are given in Table 5. The temperature dependence of k_{3t-} gave the activation parameters of Table 6 for the chloride anation of *trans*-PtCl₂.

CHLORIDE ANATION OF PtCl₃H₂O⁻

Experimental

Chemicals and apparatus were the same as in Refs. 2 and 3.

Measurements. Solutions of K₂PtCl₄ (3×10^{-3} – $5 \times 10^{-3} \text{ M}$) in HClO₄ (0.500 M) without extra chloride added, were aged over night (10–15 h) at 15, 25, or $35 \pm 0.02^\circ\text{C}$. Equal volumes of these solutions and thermostated HCl–HClO₄-solutions were mixed, so that the resulting concentration of chloride became 0.02000, 0.0500, 0.1000, or 0.2500 M. Samples were withdrawn from the reacting solution with thermostated pipettes and the absorbance was measured as a function of time at 230 nm in 1.001 or 0.501 cm cells.

Results

The rate constants k_4 and k_{4-} have been determined previously ^{2,3} from measurements of the rate of acid hydrolysis of PtCl₄²⁻ in solutions having chloride in excess. It is also possible to calculate these rate constants from measurements of the rate of the reverse chloride anation of PtCl₃⁻. This reaction may be separated from the preceding chloride anation of *cis*-PtCl₂, since the latter reaction is about 27 times faster (*vide supra*).

The aged platinum solutions used contain *cis*-PtCl₂, PtCl₃⁻ and PtCl₄²⁻. Only very small amounts of *trans*-PtCl₂ will be formed during the short aging time.⁶ When chloride is added, *cis*-PtCl₂ reacts rapidly and in practise quantitatively to PtCl₃⁻ and the consecutive slower chloride anation of PtCl₃⁻ may be followed.

The concentration of chloride, $b \text{ M}$, was chosen at least so large ($> 2 \times 10^{-2}$) that no appreciable amounts of PtCl₂ was left at equilibrium.

The first order rate constant k_{exp} may be calculated from the following eqn. (*cf.* Ref. 2, eqn. (9)):

$$\ln(e_{\infty} - e) = -k_{\text{exp}} \cdot t + \text{const.} \quad (10)$$

where

$$k_{\text{exp}} = k_4 + k_{4-} \cdot b \quad (11)$$

Table 3 gives the values of k_{exp} obtained at different b 's at the three temperatures. Plots of k_{exp} vs. b give the rate constants k_4 and k_{4-} . Fig. 9 shows

the plot for 25°C. In Table 5 the rate constants obtained are given. They agree very well with those constants calculated earlier^{2,3} from measurements of the rate of acid hydrolysis of PtCl_4^{2-} . The value of the rate constant k_{4-}

Table 3. Chloride anation of $\text{PtCl}_3\text{H}_2\text{O}^-$. The rate constant $k_{\text{exp}} = k_4 + k_{4-} \cdot b$ (s^{-1}) at different concentrations of chloride, b M. 15, 25, and 35°C. The error in k_{exp} , estimated from the graphs, is about 2 %.

| $b \times 10^3$ | $k_{\text{exp}} \times 10^5$ | | |
|-----------------|------------------------------|------|------|
| | 15°C | 25°C | 35°C |
| 20.0 | 2.91 | 9.0 | 27.5 |
| 50 | 5.5 | 17.6 | 52 |
| 100 | 10.4 | 32.0 | 92 |
| 250 | 23.9 | 74 | 207 |

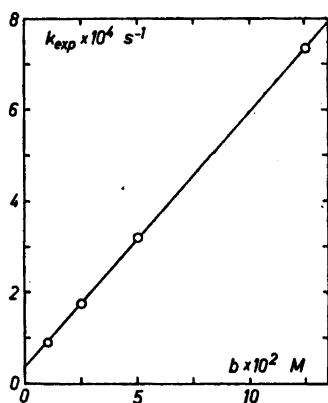


Fig. 9. Chloride anation of $\text{PtCl}_3\text{H}_2\text{O}^-$. The rate constant $k_{\text{exp}} = (k_4 + k_{4-} \cdot b)$ (s^{-1}) of eqn. (11) at different concentrations of chloride, b M. 25°C.

obtained in this paper is more accurate (error 1–2 %) than that calculated earlier,^{2,3} since the concentration of chloride could be varied in a greater interval and since the obtained changes in absorptivity were greater. The activation enthalpy and entropy given in Table 6 were calculated from the temperature dependence of the rate constant k_{4-} .

CHLORIDE ANATION OF $\text{PtCl}(\text{H}_2\text{O})_3^+$

Cation exchange separation of PtCl^+ from neutral and negatively charged species present in aged solutions of K_2PtCl_4 was described in the preceding paper.⁴ Very dilute (about 10^{-4} M) solutions of PtCl^+ , containing 3 M HClO_4 , may be obtained by this method. PtCl^+ will react with chloride to form mainly *trans*- PtCl_2 according to the *trans*-effect.⁷ The reaction to *cis*- PtCl_2 is much slower (cf. Fig. 1).

Experimental

Chemicals and apparatus were the same as in Ref. 4.

Measurements with great concentrations of chloride. PtCl^+ retained by the ion exchange column was eluted by 3 M HClO_4 as described in Ref. 4. These solutions were thermostated at $25.00 \pm 0.02^\circ\text{C}$ and then mixed with equal volumes of hydrochloric acid (2.000, 1.000, or 0.500 M). The absorbance was measured as a function of time at 230 nm in 2–4 cm cells at 25°C . The ionic strengths of the experiments are given in Table 4. Analogous experiments using a solution of K_2PtCl_4 (0.2 mM), aged in 3 M HClO_4 , and containing about 35 % *trans*- PtCl_2 , were also performed.

Measurements with small concentrations of chloride. 40 ml PtCl^+ -solution (about 10^{-4} M) was mixed with 10 ml HCl , so that the concentration of chloride in the resulting solution became 0.80, 1.00, 2.00, or 4.00 mM. The absorbance was measured *vs.* time at 230 nm in 5 cm cells at 25°C . The ionic strength of these solutions became about 2.4 M. The solutions of PtCl^+ obtained from the ion exchange experiments had such small concentrations of platinum that it was not feasible to adjust the ionic strength by dilution to the previously used value of 0.500 M.

Table 4. The rate constant k_{exp} s^{-1} of eqn. (9) calculated from experiments carried out by adding great excess of chloride to solutions containing PtCl^+ (a) and to a solution containing 35 % of the platinum as *trans*- PtCl_2 , obtained by aging a solution of K_2PtCl_4 (0.2 mM) in HClO_4 (3 M), (b). The ionic strength is I M.

| Concentration of free chloride M | $k_{\text{exp}} \times 10^5$ | | I |
|---|------------------------------|------|-----|
| | (a) | (b) | |
| 0.250 | 1.20 | 1.17 | 0.5 |
| 0.125 | 1.03 | — | 1.8 |
| 0.250 | 1.92 | 1.89 | 1.8 |
| 0.500 | 4.4 | 4.8 | 2.0 |
| 1.000 | 9.7 | 11.7 | 2.5 |

Results

Great concentrations of chloride. The results are given in Table 4. The values of the rate constant k_{exp} s^{-1} were obtained by plotting $\log(e_\infty - e)$ *vs.* t . The experiments marked (a), using solutions of PtCl^+ , gave the same rate constants at the different ionic strengths as those marked (b), using an aged solution of K_2PtCl_4 containing *trans*- PtCl_2 . The slow reaction described by this rate constant k_{exp} is in both cases the chloride anation of *trans*- PtCl_2 , studied earlier (*vide supra*). The change of $k_{\text{exp}}/[\text{Cl}^-]$ for the different experiments, apparent from the table, is due to the change of ionic strength.

Thus, these experiments show that *the slow reacting species present in aged solutions of K_2PtCl_4 can also be formed by adding chloride to solutions containing PtCl^+* . This fact strongly supports the assumption that this slow reacting species is *trans*- PtCl_2 and not, for instance, a polynuclear complex.

Small concentrations of chloride. The rate constant $k_{2\text{t}}$ $\text{s}^{-1}\text{M}^{-1}$ for the chloride anation of PtCl^+



was calculated from these measurements. The concentration of chloride, b M, was kept constant by adding it in excess to platinum. At the lowest concentrations of chloride used, 1.0 and 0.8 mM, the reverse reaction was not completely suppressed, and the percentage of platinum left as PtCl^+ at equilibrium was about 4 and 6 % in these cases. The observed first order rate constant $k_{\text{exp}} \text{ s}^{-1}$ is

$$k_{\text{exp}} = k_{2t} + k_{2t-} \cdot b \quad (13)$$

and was obtained from plots of $\log(e_{\infty} - e)$ vs. t . Fig. 10 gives some examples of such plots and Fig. 11 gives the results. The accuracy of these measurements was rather bad, because of the low concentrations and absorptivities of the platinum species and because of the small changes of absorptivity obtained. From the plot of k_{exp} vs. b , given in Fig. 11, the rate constant k_{2t-} was obtained as $(0.53 \pm 0.05) \text{ s}^{-1} \text{ M}^{-1}$ (Table 5). No reliable value of the rate constant of the reverse reaction, k_{2t} , can be obtained from the intercept because of the great experimental errors.

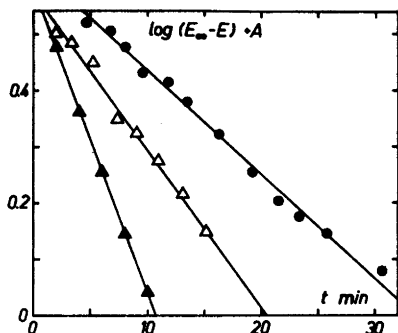


Fig. 10. Chloride anation of $\text{PtCl}(\text{H}_2\text{O})_3^+$. Plots of $\log(E_{\infty} - E) + A$ vs. t for reaction (12) at 25°C . 5 cm cell. The concentration of chloride, $b \times 10^3 \text{ M}$, was 4.00 (\blacktriangle), 2.00 (\bullet), and 1.00 (\circ). The term A added to the ordinates was 2.00 (\blacktriangle , \bullet) and 2.07 (Δ).

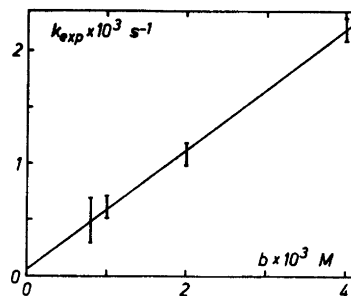


Fig. 11. Chloride anation of $\text{PtCl}(\text{H}_2\text{O})_3^+$. The observed rate constant $k_{\text{exp}} \text{ s}^{-1}$, defined by eqn. (13), as a function of the concentration of chloride, $b \text{ M}$.

Table 5. Obtained rate constants. Notations as in Fig. 1. The acid hydrolysis constants are given in s^{-1} , the chloride anation constants in $\text{s}^{-1} \text{ M}^{-1}$.

| Constant | 15°C | 25°C | 35°C |
|-----------------------|--------------------|--------------------|--------------------|
| $k_4 \times 10^5$ | 1.0 ± 0.1 | 3.6 ± 0.3 | 13 ± 1 |
| $k_4 \times 10^6$ | 1.02 ± 0.06^a | 3.7 ± 0.2^a | 12.5 ± 0.5^a |
| $k_{2-} \times 10^3$ | 0.91 ± 0.04 | 2.8 ± 0.1 | 7.8 ± 0.2 |
| $k_{2-} \times 10^3$ | 1.00 ± 0.04^a | 2.8 ± 0.1^a | 7.5 ± 0.3^a |
| $k_{2c-} \times 10^3$ | 2.57 ± 0.04 | 7.5 ± 0.2 | 20.2 ± 0.4 |
| $k_{2t-} \times 10^5$ | — | 4.6 ± 0.1 | 16.5 ± 0.5 |
| $k_{2c-} \times 10^3$ | — | 1 ± 1 | 3 ± 2 |
| k_{2t-} | — | 0.53 ± 0.05^b | — |

^a From measurements of the rate of acid hydrolysis of PtCl_4^{2-} . Refs. 2 and 3.

^b Ionic strength 2.4 M.

CONCLUSIONS

The chloride anation of *trans*-PtCl₂ follows a two term rate law—eqn. (9). The major reaction path is the direct chloride anation, which is first order with respect to both chloride and complex. The chloride independent way, which is of small importance at the high concentrations of chloride ions used at the anation experiments, arises from the reaction of *trans*-PtCl₂ via PtCl⁺ and *cis*-PtCl₂ to PtCl₃⁻. It is made possible by the rapid equilibrium between *trans*-PtCl₂ and PtCl⁺, which is due to the *trans*-effect. The reverse formation of *trans*-PtCl₂ and PtCl⁺ in aging solutions of K₂PtCl₄ may also be described by this reaction model. In this case, the formation of *trans*-PtCl₂ via *cis*-PtCl₂ and PtCl⁺ will be the major path of reaction because of the low concentration of chloride ions in these solutions (*cf.* also Ref. 6).

Table 6. Rate constants, k_{n-} s⁻¹M⁻¹, activation energies, E_a kcal mol⁻¹, activation enthalpies, ΔH^\ddagger kcal mol⁻¹, and activation entropies, ΔS^\ddagger cal mol⁻¹K⁻¹ for the chloride anation reactions at 25°C.

| Reaction | $k_{n-} \times 10^3$ | E_a | ΔH^\ddagger | ΔS^\ddagger |
|--|----------------------|-------------------|---------------------|---------------------|
| <i>cis</i> -PtCl ₂ + Cl ⁻ → PtCl ₃ ⁻ | 75 ± 2 | 18.2 | 17.7 | - 4 |
| <i>trans</i> -PtCl ₂ + Cl ⁻ → PtCl ₃ ⁻ | 0.046 ± 0.001 | 23.4 | 22.8 | - 2 |
| PtCl ₃ ⁻ + Cl ⁻ → PtCl ₄ ²⁻ | 2.8 ± 0.1 | 19.0 | 18.4 | -10 |
| » | 2.8 ± 0.1 | 17.8 ^a | 17.2 ^a | -12 ^a |
| PtCl ⁺ + Cl ⁻ → <i>cis</i> -PtCl ₂ | ~1 | ~25 | - | - |

^a From Ref. 3.

Rate laws similar to eqn. (9), having one term which is zero order with respect to the substituting ligand and one which is first order with respect to it, have been described by Langford and Gray^{8,p.22} for other ligand substitution reactions of platinum(II)-complexes. In these cases, the ligand independent term has been interpreted as arising from a reaction between one molecule of solvent and the complex. Evidently, it will not be necessary to apply such an explanation for the anation of *trans*-PtCl₂, if the model of Fig. 1 is used. A mechanism of the type described by Langford and Gray also seems unlikely in the present case since the chloride anation of *cis*-PtCl₂ is strictly second order (Figs. 4 and 5). The chloride anations of the similar platinum(II)-chloroamminecomplexes, studied by Martin and coworkers,¹¹ are also second order over all.

The reaction model used and the rate constants obtained will be discussed in detail in a subsequent paper.⁶

Professor Ido Leden promoted this work by kind interest and many valuable discussions. Mrs. Gunilla Larsson gave skilful technical assistance. *The Swedish Natural Science Research Council* supported the investigation financially. This is gratefully acknowledged.

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Received October 9, 1969.