*Inorganica Chimica Acta*, 19 (1976) 31–38

# Kinetics and Mechanism for Chloride Anation of Some Platinum(IV) Aqua Complexes in the Presence of Platinum(II)

L. I. ELDING and L. GUSTAFSON
*Division of Physical Chemistry 1, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden*
Received November 26, 1975

*Chloride anations of $PtCl_5H_2O^-$, trans-$PtCl_4(H_2O)_2$ and trans-$Pt(CN)_4ClH_2O^-$ in the presence of $PtCl_4^{2-}$ have been studied at 50° C in 1.00 M perchloric acid medium. It is shown that $PtCl_5H_2O^-$ is formed as the primary reaction product in the two last-mentioned anations. This is not compatible with the generally used mechanism for platinum(II)-catalyzed platinum (IV) substitutions, which gives $PtCl_6^{2-}$ as the direct reaction product for these two reactions. Other examples of formation of aqua complex intermediates in previously studied platinum(II)-catalyzed platinum (IV) substitutions can be found by examination of data from the literature. The chloride anation of $PtCl_5H_2O^-$ follows the rate law:*

$$rate = \frac{k' + k''[Cl^-]}{1 + k'''[Cl^-]}[PtCl_4^{2-}][PtCl_5H_2O^-]$$

*The usual interpretation of $k'''$ as the stability constant for a five-coordinate complex $PtCl_5^{3-}$ is ruled out by other experiments, which indicate a much smaller stability constant than that obtained from the kinetics. This is also supported by a stopped-flow study at 25° C in 0.5 M perchloric acid medium of the substitution of bromide by chloride in trans-$Pt(NH_3)_4Br_2$ for large concentrations of entering ligand and in the presence of $Pt(NH_3)_4^{2+}$. A modified reaction mechanism is suggested which can describe all experimental results. The primary step is the formation of a dimer complex from the platinum(IV) substrate complex and the simple platinum(II) complex, hydrated in the axial positions. This dimer might decompose directly to a platinum(II) complex and a platinum(IV) aqua complex. Alternatively, it might react with the incoming ligand to form a new dinuclear complex, which decomposes to the platinum(II) complex and the substituted platinum(IV) complex.*

## Introduction

The generally accepted mechanism for substitution reactions of platinum(IV) complexes in the presence of platinum(II) was postulated in 1958 by Basolo, Pearson *et al.*:[1–3]

$$Pt(II) + X \rightleftarrows Pt(II){-}X \text{ (rapid, equil. constant } K) \quad (1)$$

$$Y{-}Pt(IV){-}Z + Pt(II){-}X \rightleftarrows Y{-}Pt{-}Z{-}Pt{-}X \quad (2)$$

$$Y{-}Pt{-}Z{-}Pt{-}X \rightleftarrows Y{-}Pt(II) + Z{-}Pt(IV){-}X \quad (3)$$

$$Y{-}Pt(II) \rightleftarrows Y + Pt(II) \quad (4)$$

The four in-plane ligands of the platinum(II) and platinum(IV) complexes have been omitted. Z and Y denote two ligands in *trans*-position to each other. The rate determining step is reaction (2) or (3), with a rate constant $k$. The mechanism gives a reaction rate

$$Rate = \frac{kK[X][Pt(II)]}{1+K[X]}[Pt(IV)] \quad (5)$$

If $K[X] \ll 1$, *i.e.* if the concentration of the entering ligand and/or the formation constant for the five-coordinate platinum(II) complex is small, eqn. (5) is reduced to

$$Rate = kK[X][Pt(II)][Pt(IV)] \quad (6)$$

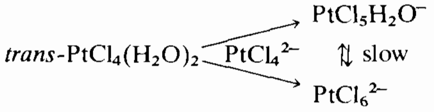
Eqns. (5) and (6) agree with experimental findings.[4] Since the mechanism implies an exchange of platinum,[3,5] the platinum(II) complex should be regarded as a reactant, not as a catalyst.

The mechanism postulates participation of five-coordinate platinum(II) complexes. Peloso *et al.*[6–9] have demonstrated the existence of such complexes between cationic platinum(II) species and negatively charged ligands in nonaqueous solvents, where the formation of ion pairs is more extensive than in aqueous solution. In these cases the experimental rate laws agree with eqn. (5). Agreement between the equilibrium constants $K$ for reaction (1) calculated independently from kinetics and equilibria is a necessary – but not sufficient – condition for the mechanism (1)–(4).

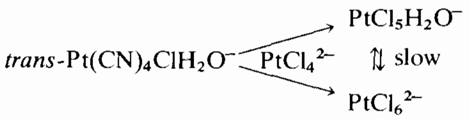
Orginally, the mechanism (1)–(4) was used only for addition of anions to cationic platinum(II) complexes, such as $Pt(NH_3)_4^{2+}$ and $Pt(en)_2^{2+}$. But there are several examples in recent literature where the model has also been used for addition of halide to anionic platinum(II) substrates, *e.g.* $Pt(CN)_4^{2-}$ [10–12] and $Pt(NO_2)_4^{2-}$. [10]

The present paper describes the kinetics for reactions (7), (8) and (9) in the presence of hydrochloric acid and tetrachloroplatinate(II):

$$\text{PtCl}_5\text{H}_2\text{O}^- + \text{Cl}^- \xrightleftharpoons{\text{PtCl}_4^{2-}} \text{PtCl}_6^{2-} + \text{H}_2\text{O} \tag{7}$$



$$\mathit{trans}\text{-PtCl}_4(\text{H}_2\text{O})_2 \xrightarrow{\text{PtCl}_4^{2-}} \begin{array}{c} \text{PtCl}_5\text{H}_2\text{O}^- \\ \updownarrow \text{ slow} \\ \text{PtCl}_6^{2-} \end{array} \tag{8}$$



$$\mathit{trans}\text{-Pt(CN)}_4\text{ClH}_2\text{O}^- \xrightarrow{\text{PtCl}_4^{2-}} \begin{array}{c} \text{PtCl}_5\text{H}_2\text{O}^- \\ \updownarrow \text{ slow} \\ \text{PtCl}_6^{2-} \end{array} \tag{9}$$

The experiments indicate that $PtCl_5H_2O^-$ is formed as an intermediate in large concentrations both in reaction (8) and (9). This is not compatible with the mechanism (1)–(4). The reaction between a five-coordinate complex $PtCl_5^{3-}$ and the platinum(IV) complex should give $PtCl_6^{2-}$ directly in both cases, since water is known to be a poor bridging ligand,[4] *i.e.* $Z \neq H_2O$ in (2) and (3).

The appearance of aqua complexes as intermediates necessitates a modification of the reaction mechanism (1)–(4). A tentative model is given in Figure 1. The primary process is a direct reaction between the platinum(IV) complex and the platinum(II) complex, $PtCl_4^{2-}$ (hydrated in the axial positions). This mechanism gives a rate expression of the same mathematical form as that obtained from reactions (1)–(4). Our kinetic results for reaction (7) also give quantitative support to the mechanism in Figure 1. The idea of water as the fifth ligand in the platinum(II) complex instead of halide has been previously suggested by Mason.[10]

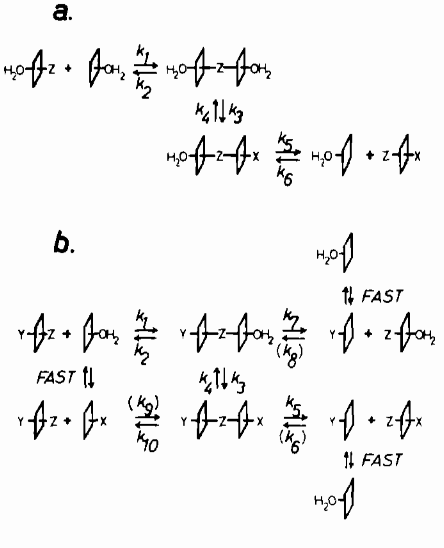


Figure 1. Suggested reaction model: (*a*) for simple anation reactions where the four in-plane ligands of the platinum(II) complex are identical with those of the platinum(IV) complex, and (*b*) for substitution reactions in general. Reactions which involve five-coordinate platinum(II) complexes as reactants are neglected. Their rate constants have been written within parentheses.

The possibility of a Pt(III)-catalysis as described by Rich and Taube[13] as an alternative to the suggested mechanism will be discussed in the final part of the paper.

Some studies on the hydrolysis reactions of $PtCl_6^{2-}$ have been published previously.[14–20] As early as 1920, Archibald[14] reported that the rates of chloride anation for the hydrolysis products of $PtCl_6^{2-}$ were influenced by light and catalysts, much in the same way as the hydrolysis rates. Since that time, only one quantitative investigation on the kinetics of these anations has been reported.[20]

We have also followed reaction (10) in the presence of $Pt(NH_3)_4^{2+}$ for large concentrations of entering chloride ligand, in order to try to find kinetic evidence for the existence in aqueous solution of the five-coordinate complex $Pt(NH_3)_4Cl^+$, postulated in the mechanism (1)–(4):

$$\mathit{trans}\text{-Pt(NH}_3)_4\text{Br}_2^{2+} + \text{Cl}^- \rightarrow \mathit{trans}\text{-Pt(NH}_3)_4\text{BrCl}^{2+} + \text{Br}^- \tag{10}$$

## Experimental

### *Chemicals*

Potassium tetrachloroplatinate(II) (Degussa or Johnson and Matthey), potassium hexachloroplatinate(IV) (Baker's), potassium tetracyanoplatinate(II) (Johnson and Matthey) and tetrammineplatinum(II) chloride (Johnson and Matthey) were used without further purification. All other chemicals were reagent grade.

Solutions of $PtCl_5H_2O^-$ were prepared either by aging solutions of potassium hexachloroplatinate(IV) (about 0.7 m*M*) in 1.00*M* perchloric acid solution in UV light from a quartz lamp for about 2 h, or by oxidation of tetrachloroplatinate(II) (0.6 m*M* to 1.6 m*M*) in 1.00*M* perchloric acid solution with chlorine and subsequent evaporation of the excess chlorine by flushing with nitrogen.[21]

Solutions of *trans*-$Pt(CN)_4ClH_2O^-$ were prepared by oxidation of tetracyanoplatinate(II) (0.5 m*M*) in 1.00*M* perchloric acid with chlorine.

The potassium salt of *trans*-$PtCl_4(OH)_2^{2-}$ was synthesized according to ref. 22 by oxidation of tetrachloroplatinate(II) with hydrogen peroxide. Dissolution of this salt in 1.00*M* perchloric acid gave *trans*-$PtCl_4(H_2O)_2$.

The bromide salt of *trans*-$Pt(NH_3)_4Br_2^{2+}$ was prepared by oxidation of tetrammineplatinum(II) chloride in hydrobromic acid solution with bromine.[23]

### *Apparatus*

Spectra were recorded by a Cary 14 recording spectrophotometer. Halide exchange in $Pt(NH_3)_4Br_2^{2+}$ was followed using a modified Durrum Gibson stopped-flow instrument.[24] For other kinetic runs, a Zeiss Quartz Spectrophotometer PMQ II was used.

### *Reactions (7), (8) and (9)*

The reactions were started by mixing one solution containing $PtCl_4^{2-}$ ($6\times10^{-4}M$ to $4\times10^{-3}M$ for reactions (7) and (8), $5\times10^{-3}M$ for reaction (9)) and hydrochloric acid ($0.2M$ to $1.0M$) and another, containing platinum(IV) complex ($6\times10^{-4}M$ to $16\times10^{-4}M$ for reactions (7) and (8), $5\times10^{-4}M$ for reaction (9)) at (50.0 ± 0.2)° C. The concentrations of chloride and platinum(II) complex were always large enough to give pseudo first-order kinetics. The large concentrations of platinum(II) complex also made small impurities of platinum(II) in the platinum(IV) salts negligible. The reacting solutions were protected from illumination by keeping them in bottles wrapped in aluminum foil in closed water thermostats. All handling was performed in red light of low intensity. Samples were withdrawn and the absorbance measured at 264 nm, near the absorption peak of $PtCl_6^{2-}$. All measurements were performed using blanks containing $PtCl_4^{2-}$ and chloride.

The ionic strength and hydrogen ion concentration of all solutions were $1.00M$ and the supporting electrolyte perchloric acid. The hydrogen ion concentration of $1.00M$ was sufficient to suppress protolysis of the aqua complexes since $pK_{a_1}$ for *trans*-$PtCl_4(H_2O)_2$ is 1.9[22] and $pK_a$ for $PtCl_5H_2O^-$ is 3.8.[18]

### *Halide Substitution in $Pt(NH_3)_4Br_2^{2+}$*

One of the solutions mixed in the stopped-flow instrument contained $Pt(NH_3)_4^{2+}$ ($2.04\times10^{-3}M$) and chloride ($0.100$–$0.500M$), the other *trans*-$Pt(NH_3)_4Br_2^{2+}$ ($3.48\times10^{-5}M$). The ionic strength was maintained at $0.50M$ by perchloric acid. The temperature was (25.0 ± 0.1)° C. The experimental rate constants given in Figure 7 were calculated by a least-squares program from the transmittance *vs*. time curves.

## Results

### *Reaction (7)*

The start solutions of $PtCl_5H_2O^-$ were prepared by oxidation of $PtCl_4^{2-}$ with chlorine or by aging of $PtCl_6^{2-}$. Reaction (7) was also obtained as a subsequent process in reactions (8) and (9). All results are given in Table I. The rate constants were obtained from ordinary first-order plots. The experimental values of the final absorptivity for each kinetic run varied with the concentration of chloride. This indicates that the reactions do not go to completion, *i.e.* the reaction product is an equilibrium mixture of $PtCl_5H_2O^-$ and $PtCl_6^{2-}$.

TABLE I. Rate Constants for Chloride Anation of $PtCl_5H_2O^-$. The total concentration of platinum(IV) was $6.3\times10^{-5}M$. $PtCl_5H_2O^-$ was obtained from: *a* $Cl_2$-oxidized $PtCl_4^{2-}$ solutions, *b* anation of *trans*-$PtCl_4(H_2O)_2$, *c* aged $PtCl_6^{2-}$ solutions, and *d* reaction (9). The errors are given as 1σ.

| | $[Cl^-]/M$ | $[PtCl_4^{2-}]\times10^3/M$ | $k_{exp}\times10^5/s^{-1}$ |
|---|---|---|---|
| a | 0.200 | 1.01 | 5.4 ± 0.1 |
| a | 0.200 | 2.01 | 8.2 ± 0.1 |
| a | 0.200 | 4.03 | 17.6 ± 0.2 |
| a | 0.308 | 2.91 | 16.4 ± 0.4 |
| a | 0.346 | 3.86 | 22.8 ± 0.6 |
| a | 0.400 | 1.01 | 7.2 ± 0.1 |
| a | 0.400 | 2.01 | 13.6 ± 0.1 |
| a | 0.400 | 4.03 | 26.1 ± 0.1 |
| a | 0.442 | 1.93 | 14.2 ± 0.3 |
| a | 0.500 | 3.86 | 32.6 ± 0.2 |
| a | 0.600 | 1.01 | 9.5 ± 0.1 |
| a | 0.600 | 2.01 | 18.0 ± 0.5 |
| a | 0.600 | 4.03 | 36.5 ± 0.7 |
| a | 0.688 | 0.97 | 10.0 ± 0.3 |
| a | 0.702 | 1.93 | 17.7 ± 0.2 |
| a | 0.716 | 2.91 | 28.3 ± 0.5 |
| a | 0.731 | 3.86 | 37.1 ± 0.2 |
| a | 0.880 | 2.91 | 30.0 ± 0.5 |
| a | 0.885 | 3.86 | 42.8 ± 0.3 |
| a | 0.900 | 1.01 | 12.4 ± 0.1 |
| a | 0.900 | 2.01 | 22.6 ± 0.5 |
| a | 0.960 | 3.86 | 46 ± 1 |
| b | 0.615 | 1.93 | 17.4 ± 0.5 |
| b | 0.635 | 2.91 | 28.0 ± 0.5 |
| b | 0.654 | 3.86 | 34.5 ± 0.3 |
| b | 0.960 | 0.58 | 7.5 ± 0.1 |
| b | 0.960 | 0.97 | 11.0 ± 0.4 |
| b | 0.960 | 1.93 | 20.2 ± 0.1 |
| b | 0.960 | 2.91 | 33.5 ± 0.5 |
| b | 0.960 | 3.86 | 42 ± 1 |
| c | 0.564 | 0.92 | 8.6 ± 0.1 |
| c | 0.582 | 1.83 | 17.3 ± 0.1 |
| c | 0.909 | 0.92 | 10.8 ± 0.2 |
| c | 0.909 | 1.83 | 21.6 ± 0.4 |
| d | 0.300 | 5.03 | 24.9 ± 0.7 |
| d | 0.400 | 5.03 | 34.6 ± 0.8 |
| d | 0.500 | 5.03 | 36 ± 1 |
| d | 0.700 | 5.03 | 44.4 ± 0.4 |
| d | 0.900 | 5.03 | 55 ± 2 |

Figure 2 shows that the observed rate constant is a linear function of the concentration of platinum(II) for each concentration of chloride used. There is a

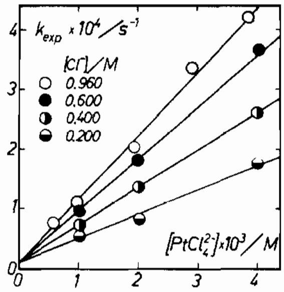


Figure 2. Chloride anation of $PtCl_5H_2O^-$. The observed rate constant, $k_{exp}$, as a function of the concentration of $PtCl_4^{2-}$ for different concentrations of chloride.

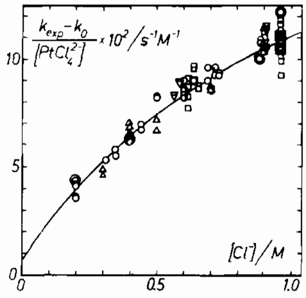


Figure 3. Chloride anation of $PtCl_5H_2O^-$. $(k_{exp}-k_0)/[PtCl_4^{2-}]$ as a function of chloride concentration. $k_0$ was obtained from the intercept in Figure 2. The curve was calculated from the experiments *a* (○) and *b* (□) in Table I. For comparison, the experiments c (▽) and *d* (△) have also been included.

small intercept, $k_0$, which might indicate a reaction path independent of platinum(II). Experiments were performed to study this "uncatalyzed" path. But since the reactions are very slow in the absence of platinum (II), and therefore relatively more sensitive to illumination and trace amounts of catalysts, these experiments were not reproducible enough to verify such a path.

The graph shown in Figure 3 corresponds to the following expression for the experimental rate constant:

$$k_{exp}-k_0 = \frac{k'+k''[Cl^-]}{1+k'''[Cl^-]}[PtCl_4^{2-}] \qquad (11)$$

By a least-squares analysis, using the Univac 1108 computer, the following values of the parameters were calculated from experiments *a* and *b* in Table I:

$k_0 = (1.0\pm0.5)s^{-1}$
$k' = (6\pm4)\cdot10^{-3}s^{-1}M^{-1}$
$k'' = (0.20\pm0.02)s^{-1}M^{-2}$
$k''' = (0.9\pm0.2)M^{-1}$

The stepwise stability constant $K_6$ for $PtCl_6^{2-}$ is equal to $k''/k' = (30\pm20)M^{-1}$. This value agrees satisfactorily with previous determinations.[18,25,36]

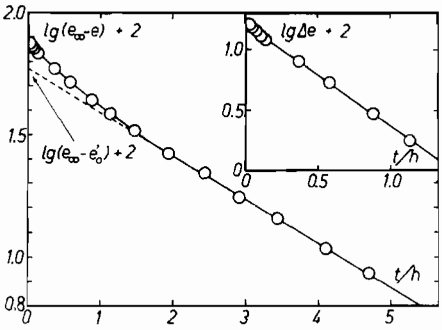


Figure 4. $lg(e_\infty-e)$ *vs.* *t* for chloride anation of *trans*-$PtCl_4(H_2O)_2$. The total concentration of platinum(IV) was $6.5\times10^{-5}M$, of chloride $0.960M$, and of platinum(II) $0.97\times10^{-3}M$. From the linear part of the curve, the rate constant for the slow reaction was obtained as $11.4\times10^{-5}$ $s^{-1}$. The rate constant for the fast reaction was calculated from the small plot as $5.4\times10^{-4}$ $s^{-1}$. $\Delta e$ denotes the difference in absorptivity between the experimental curve and the extrapolated, dashed line.

### *Reaction (8)*

The potassium salt of *trans*-$PtCl_4(OH)_2$, dissolved in $1.00M$ perchloric acid was used for these experiments. Logarithmic first-order plots like that shown in Figure 4 indicate two reactions. The slow process was identified as reaction (7) and the rate constants, calculated from the linear parts of the plots, are given in Table I. Thus, $PtCl_5H_2O^-$ is formed during the fast reaction.

The amount of $PtCl_6^{2-}$ formed as a product in the slow reaction can be calculated from the extrapolated absorptivity $(e_\infty-e_0')$ (*vide* Figure 4) and the molar absorptivities of $PtCl_6^{2-}$ (24800 $cm^{-1}M^{-1}$) and $PtCl_5H_2O^-$ (11800 $cm^{-1}M^{-1}$). This amount was always less

TABLE II. Rate Constants and Product Distribution for Chloride Anation of *trans*-$PtCl_4(H_2O)_2$. The platinum(IV) concentration was $6.5\times10^{-5}M$. The errors are given as 1σ.

| $[Cl^-]/M$ | $[PtCl_4^{2-}]\times10^3/M$ | $k_{exp}\times10^4/s^{-1}$ | $[PtCl_6^{2-}]_{extr}/[PtCl_5H_2O^-]_{extr}$ |
|---|---|---|---|
| 0.215 | 0.58 | 2.9 ± 0.3 | 0.12 ± 0.01 |
| 0.231 | 0.97 | 4.8 ± 0.3 | – |
| 0.270 | 1.93 | 9.2 ± 0.1 | – |
| 0.308 | 2.91 | 14.2 ± 0.9 | 0.24 ± 0.02 |
| 0.365 | 1.93 | – | 0.13 ± 0.01 |
| 0.588 | 0.58 | 3.0 ± 0.1 | 0.20 ± 0.02 |
| 0.596 | 0.97 | 5.6 ± 0.2 | 0.26 ± 0.02 |
| 0.615 | 1.93 | 10.8 ± 0.2 | 0.22 ± 0.01 |
| 0.635 | 2.91 | – | 0.27 ± 0.03 |
| 0.654 | 3.86 | – | 0.16 ± 0.02 |
| 0.960 | 0.58 | 3.3 ± 0.1 | 0.39 ± 0.04 |
| 0.960 | 0.97 | 6.1 ± 0.3 | 0.34 ± 0.02 |
| 0.960 | 1.93 | 11.0 ± 0.4 | 0.32 ± 0.01 |
| 0.960 | 2.91 | 17.9 ± 0.8 | – |

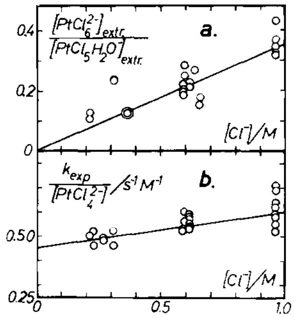


Figure 5. Chloride anation of *trans*-$PtCl_4(H_2O)_2$. (*a*) The quotient between the concentrations of the direct reaction products, and (*b*) $k_{exp}/[PtCl_4^{2-}]$ as functions of chloride concentration.

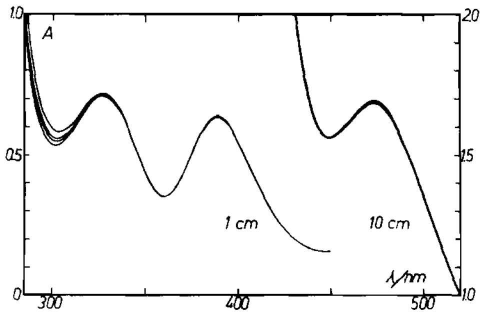


Figure 6. Absorption spectra of four neutral solutions of $PtCl_4^{2-}$ with excess chloride. The concentration of platinum was $1.03 \times 10^{-2} M$, and of chloride 0.50, 1.00, 1.50 and 3.00 *M*. The spectra coincide except for a small deviation in the region 320 to 280 nm. The ionic strength was 5.00 *M*, and the supporting electrolyte sodium perchlorate. The path length was 1.001 and 10.00 cm.

than the total amount of $PtCl_6^{2-}$ at the final equilibrium. Therefore, some $PtCl_6^{2-}$ must also be formed during the fast reaction, so we can write the overall process as formula (8).

The amounts of $PtCl_6^{2-}$ and $PtCl_5H_2O^-$ formed as products in the fast reaction were calculated from $\lg(\epsilon_\infty - \epsilon_0')$, $\epsilon_\infty$ and the molar absorptivities for $PtCl_6^{2-}$ and $PtCl_5H_2O^-$. The ratios between the concentrations of the products are given in Table II. These should be equal to the ratio between the rate constants for the two parallel paths of the fast reaction.[26] In Figure 5a, the product concentration ratios have been plotted *vs.* the concentration of chloride, which gives a straight line through the origin with slope $(0.35 \pm 0.05) M^{-1}$.

The experimental rate constant for the fast reaction was calculated from differences between the experimental curve and the extrapolated line in plots like Figure 4. The results are given in Table II. As indicated by Figure 5b, the observed rate constant can be written

$$k_{exp} = (k' + k''[Cl^-])[PtCl_4^{2-}] \qquad (12)$$

The parameters $k'$ and $k''$ were obtained from a least-squares calculation as:

$$k' = (0.45 \pm 0.02)\, s^{-1} M^{-1}$$
$$k'' = (0.15 \pm 0.03)\, s^{-1} M^{-2}$$

The ratio $k''/k' = (0.33 \pm 0.07) M^{-1}$ agrees with the slope for the line in Figure 5a. Thus, $k'$ is the rate constant for the formation of $PtCl_5H_2O^-$ and $k''$ that for the direct formation of $PtCl_6^{2-}$ from *trans*-$PtCl_4(H_2O)_2$.

*Reaction (9)*

These experiments gave reaction (7) as the rate determining step. The observed rate constants are given in Table I. Thus, $PtCl_5H_2O^-$ appears as an intermediate in large concentrations in reaction (9).

## Discussion

### *Five-coordinate Platinum(II) Complexes*

The experimental expression (11) for the rate constant for reaction (7) is of the same mathematical form as that expected from the mechanism (1)–(4) for a reversible process:

$$k_{exp} = \frac{k' + kK[Cl^-]}{1 + K[Cl^-]} [PtCl_4^{2-}] \qquad (13)$$

Thus, the parameter $k''' = (0.9 \pm 0.2) M^{-1}$, obtained from the kinetic measurements, should be identified with the equilibrium constant *K* for the reaction

$$PtCl_4^{2-} + Cl^- \rightleftarrows PtCl_5^{3-} \qquad (14)$$

However, the large value of $0.9 M^{-1}$ for this equilibrium constant is not consistent with other experimental observations:

*(i)*. Figure 6 shows spectra of aqueous solutions of tetrachloroplatinate(II) with excess chloride. If the stability constant of $PtCl_5^{3-}$ were $0.9 M^{-1}$, these solutions should contain between 30% and 70% of the platinum as $PtCl_5^{3-}$, if ionic strength effects on the equilibrium are neglected. The changes of the spectra are much too small to account for this large variation of concentration, unless the absorption spectra $PtCl_4^{2-}$ and $PtCl_5^{3-}$ are very similar.

*(ii)*. The rate expression for anation reactions of platinum(II) complexes in aqueous solution should deviate from the first-order dependence on the entering ligand, if substantial amounts of five-coordinate platinum(II) complexes were formed.[27] Such behavior has never been reported, not even when the entering ligand and substrate complex are oppositely charged. For instance, the anation

$$Pt(H_2O)_4^{2+} + X^- \rightarrow PtX(H_2O)_3^+ + H_2O \qquad (15)$$

is strictly first-order with respect to entering ligand X = Cl, Br up to concentrations of 0.5 *M*.[28] The same is valid for the substrates *trans*-$PtX_2(H_2O)_2$[29] and the corresponding palladium complexes.[30]

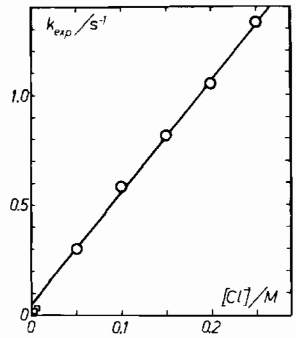


Figure 7. The observed rate constant for reaction (10) as a function of the concentration of chloride. The concentration of platinum(IV) was $1.74\times10^{-5}M$, of platinum(II) $1.02\times10^{-3}M$ and of hydrogen ions $0.50M$ (○). Ionic strength $0.50M$. Rettew and Johnson's[31] two previous experiments on the same reaction have also been included (□). The deviation of their points from our results indicates that ionic strength and/or hydrogen ion concentration affect the rates.

*(iii)*. Reactions between platinum(IV) complexes and halide ions in the presence of *positively* charged platinum(II) complexes should be more favourable for detection of five-coordination than reactions with the doubly negatively charged $PtCl_4^{2-}$. But the plot for reaction (10) shown in Figure 7 is strictly linear up to chloride concentrations of $0.25M$. No evidence for saturation like the curvature in Figure 3 can be observed. Therefore, the formation constant for $Pt(NH_3)_4Cl^+$ must be less than about $0.1M^{-1}$ which is not consistent with a value of $0.9M^{-1}$ for $PtCl_5^{3-}$.

### *Aqua Complexes as Intermediates*

The results described indicate that $PtCl_5H_2O^-$ is obtained as a primary product in reactions (8) and (9). More examples of formation of aqua complex intermediates in Pt(IV) substitutions catalysed by both cationic and anionic platinum(II) species can be found by examination of data from the literature. For instance, the similarity of the rate constants for the halide substitutions and anations in the presence of $Pt(NH_3)_4^{2+}$ listed in Table III indicates that the primary step in the halide substitutions most probably is a fast formation of an aqua complex, followed by a rate determining halide anation of this species.

For the substitution reaction

$$Pt(CN)_4Br_2^{2-} + Cl^- \rightarrow Pt(CN)_4BrCl^{2-} + Br^- \qquad (16)$$

studied in the presence of $Pt(CN)_4^{2-}$, Mason[10] found a rate constant

$$k_{exp} = (k_1 + k_2[Cl^-])[Pt(CN)_4^{2-}] \qquad (17)$$

*i.e.* a relation similar to eqn. (12) for the anation of *trans*-$PtCl_4(H_2O)_2$. The chloride independent term was interpreted in a similar way, *i.e.* as a formation of an aqua complex in a primary reaction step.

### *Mechanism*

Since the formation constant for $PtCl_5^{3-}$ is probably much too small to be identified with the parameter $0.9M^{-1}$ in the experimental expression (11) for the rate constant for reaction (7), another mechanism than (1)–(4) must be operating. Obviously, the incoming ligand enters the complex *after* the formation of the bridged complex. Thus, the simple hydrated platinum (II) complex, not the five-coordinate platinum(II) species $PtCl_5^{3-}$ is the reactant in this case. For negatively charged platinum(II) complexes, electrostatic reasons support this view. However, the occurrence of aqua complex intermediates for the reactions in Table III with the cationic $Pt(NH_3)_4^{2+}$ indicates that the hydrated platinum(II) complex is a reactant also in these cases. Peloso's results[8] for nonaqueous solvents are compatible with both models: the factor $[Pt(II)]_{tot}/(1 + K[X])$ which appears in his rate expression gives the concentration of four-coordinate platinum(II) complex, which is the reactant according to the model in Figure 1.

For simple reversible anations like reaction (7) the mechanism in Figure 1a gives

$$k_{exp} = \frac{\dfrac{k_4k_6}{k_4+k_5} + \dfrac{k_1k_3k_5[X]}{k_2(k_4+k_5)}}{1 + \dfrac{k_3k_5[X]}{k_2(k_4+k_5)}}[Pt(II)] \qquad (18)$$

if steady state concentrations are assumed for the bridged complexes. This expression agrees with the ex-

TABLE III. Third Order Rate Constants $k_{exp}$ for Some Reactions in the Presence of $Pt(NH_3)_4^{2+}$. The rate constants for the anations have been calculated for the same pH as was used for the substitutions.

| Complex | Entering Ligand | $[H^+]\times10^3/M$ | $k_{exp}/s^{-1}M^{-2}$ | $I/M$ | Ref. |
|---|---|---|---|---|---|
| $Pt(NH_3)_4ClBr^{2+}$ | $Cl^-$ | 5 | 6.3 | 0.20 | 31 |
| $Pt(NH_3)_4ClH_2O^{3+}$ | $Cl^-$ | 27–60 | 8.5[a] | 0.50 | 32 |
| $Pt(NH_3)_4ClBr^{2+}$ | $Br^-$ | 5 | $1.9\times10^4$ | 0.20 | 31 |
| $Pt(NH_3)_4BrH_2O^{3+}$ | $Br^-$ | 10–44 | $2.1\times10^4$ [a] | 0.50 | 12 |

[a] For $[H^+] = 5\times10^{-3}M$.

perimental rate law (11), but of course the parameters $k'$, $k''$ and $k'''$ in eqn. (11) now have another physical meaning than in eqn. (13). However, the ratio $k''/k'$ still means the stepwise stability constant $K_6$ for $PtCl_6^{2-}$.

For substitutions where the leaving ligand is not the solvent, or for reactions where the four in-plane ligands in the platinum(IV) complex and platinum(II) complex are not identical, the model in Figure 1b can be used. In these cases, the primary product can be either the aqua complex, or the final substituted complex, or a mixture of these two species. If the concentration of five-coordinate platinum(II) complex is assumed to be small, the reactions described by $k_6$, $k_8$ and $k_9$ can be neglected. With steady state assumptions for the dinuclear species, the rate constant for formation of the products is then given by

$$k_{exp} = k_1 \frac{k_7(k_4+k_5+k_{10}) + k_3 \cdot k_5[X]}{k_4(k_2+k_7) + (k_5+k_{10})(k_2+k_7+k_3[X])} \times [Pt(II)] \quad (19)$$

This is the general expression for the rate constant when both aqua complex and substituted complex are formed, and agrees with the observed rate constant for the chloride anation of *trans*-$PtCl_4(H_2O)_2$, eqn. (12), if $k_3[X] \ll (k_2+k_7)$.[33]

For $k_3[X] \ll k_7$ the aqua complex is formed exclusively with a rate constant

$$k_{exp} = \frac{k_1 k_7}{k_2+k_7}[Pt(II)] \quad (20)$$

If $k_7 \ll k_3[X]$, only the substituted complex Z–Pt(IV)–X is formed, provided that $k_4$ and $k_{10}$ are not very large compared to $k_5$. The rate constant is then given by

$$k_{exp} = \frac{k_3 k_5[X][Pt(II)]}{k_2 k_4 + (k_5+k_{10})(k_2+k_3[X])} \quad (21)$$

If $k_3[X] \ll k_2$ this expression agrees with that generally obtained for these substitution reactions

$$k_{exp} = k''[X][Pt(II)] \quad (22)$$

For some reactions, the experimental rate expressions are consistent with the model only if $k_3[X] \ll k_2$ or $k_3[X] \ll (k_2+k_7)$. In other reactions, *e.g.* the chloride anation of $PtCl_5H_2O^-$, $k_3[X]$ must instead be comparable to $k_2$ (*cf.* eqn. (18)). These differences might depend on the relative electronegativities of the ligands in the bridged complex.

Rich and Taube, in a classical paper,[13] studied the exchange of chloride between $PtCl_6^{2-}$ and free chloride ions and found it to be rapid in solutions without inhibitors present. This rapid exchange was attributed to catalysis by labile Pt(III) chloro complexes. Addition of inhibitors destroyed Pt(III) and quenched the reaction. The anation of $PtCl_5H_2O^-$ studied in the present paper is extremely slow in the dark, if not large concentrations of $PtCl_4^{2-}$ are present. Even in this case, the half-lives for the reactions studied were generally several hours at 50° C (*cf.* Table I).

On the other hand, if a solution of $PtCl_5H_2O^-$ with, say, 500 m*M* chloride is illuminated by UV light, a rapid anation to $PtCl_6^{2-}$ occurs, similar in rate to the Pt(III)-catalyzed photoexchange observed by Rich and Taube. The rate of the dark reaction is unaffected by addition of small concentrations of Fe(III).

We therefore conclude that the mechanism for the dark reaction does not probably involve Pt(III)-catalysis. Moreover, we have not succeeded in deducing any rate law, which conforms to the experimental eqn. (11) from mechanisms involving Pt(III)-species. These generally give rate expressions containing square-root terms (*cf.* also ref. 2, p. 208).

## Conclusions

The possibility of water as the fifth ligand instead of a halide is supported by the formation of aqua complexes as reaction products, both when anionic and cationic platinum(II) complexes are used. The rate law for the anation of $PtCl_5H_2O^-$ (eqn. (11)) and the large value of the parameter $k'''$ compared to the stability constant of $PtCl_5^{3-}$, indicate that the halide ligand enters the complex after the formation of a dinuclear aqua complex according to Figure 1. We will subsequently report rate laws for the anations of $PtBr_5H_2O^-$ [34] and *trans*-$Pt(CN)_4ClH_2O^-$ [35] which have the same form as eqn. (11).

When eqn. (5) with $k''' = K$ or eqn. (6) describes the kinetics, the model in Figure 1 is kinetically indistinguishable from the Basolo, Pearson scheme (1)–(4). Only when the parameter $k'''$ differs from the equilibrium constant K of reaction (1) can the mechanism (1)–(4) be ruled out.

## Acknowledgments

We are indebted to professor Ido Leden for valuable advice and stimulating discussions, to Ingegerd Lind, F.M., for experimental assistance, and to the *Swedish Natural Science Research Council* for financial support.

## References and Notes

1 F. Basolo, P.H. Wilks, R.G. Pearson and R.G. Wilkins, *J. Inorg. Nucl. Chem.*, *6*, 161 (1958).
2 F. Basolo, A.F. Messing, P.H. Wilks, R.G. Wilkins and R.G. Pearson, *J. Inorg. Nucl. Chem.*, *8*, 203 (1958).
3 F. Basolo, M.L. Morris and R.G. Pearson, *Disc. Faraday Soc.*, *29*, 80 (1960).

4 W.R. Mason, *Coord. Chem. Rev., 7,* 241 (1972).

5 L.T. Cox, S.B. Collins and D.S. Martin, Jr., *J. Inorg. Nucl. Chem., 17,* 383 (1961).

6 G. Dolcetti, A. Peloso and L. Sindellari, *Gazz. Chim. Ital., 96,* 1648 (1966).

7 A. Peloso and G. Dolcetti, *Coord. Chem. Rev., 1,* 100 (1966).

8 A. Peloso and R. Ettorre, *J. Chem. Soc. A,* 2253 (1968).

9 A. Peloso, *Gazz. Chim. Ital., 99,* 723 (1969), *99,* 1025 (1969), and *100,* 188 (1970).

10 W.R. Mason, *Inorg. Chem., 8,* 1756 (1969).

11 W.R. Mason, *Inorg. Chem., 9,* 1528 (1970).

12 K.A. Morgan and M.M. Jones, *J. Inorg. Nucl. Chem., 34,* 275 (1972).

13 R.L. Rich and H. Taube, *J. Am. Chem. Soc., 76,* 2608 (1954).

14 E.H. Archibald, *J. Chem. Soc., 117,* 1104 (1920).

15 R. Dreyer and I. Dreyer, *Z. Chem., 3,* 151 (1963).

16 R. Dreyer, I. Dreyer and D. Rettig, *Z. Phys. Chem., 224,* 199 (1963).

17 N.M. Nikolaeva, B.V. Ptitsyn and E.D. Pastukhova, *Russ. J. Inorg. Chem., 10,* 574 (1965).

18 C.M. Davidson and R.F. Jameson, *Trans. Faraday. Soc., 61,* 2462 (1965).

19 V.M. Shulman and V.I. Dubinskii, *Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 1,* 25 (1966).

20 S. Yamasaki, T. Kumamaru and I. Nakamori, *Kyushu Daigaku Kogaku Shuho, 44,* 82 (1971); *C.A., 77,* 66631c (1972).

21 L.E. Cox, D.G. Peters and E.L. Whery, *J. Inorg. Nucl. Chem., 34,* 297 (1972).

22 L.E. Cox and D.G. Peters, *Inorg. Chem., 9,* 1927 (1970).

23 *Gmelin's Handbuch der Anorganischen Chemie, 68 D,* 501 (1957).

24 L.I. Elding, *Inorg. Chim. Acta, 6,* 683 (1972).

25 O. Ginstrup, *Acta Chem. Scand., 26,* 1527 (1972).

26 A.A. Frost and R.G. Pearson, "Kinetics and Mechanism", Wiley, 1961, p. 161.

27 C.H. Langford and H.B. Gray, "Ligand Substitution Processes", New York, 1965, p. 12, 44.

28 L.I. Elding, to be published.

29 L.I. Elding, *Acta Chem. Scand., 24,* 1341, 2557 (1970).

30 L.I. Elding, *Inorg. Chim. Acta, 7,* 581 (1973).

31 R.R. Rettew and R.C. Johnson, *Inorg. Chem., 4,* 1565 (1965).

32 M.M. Jones and K.A. Morgan, *J. Inorg. Nucl. Chem., 34,* 259 (1972).

33 The $PtCl_4^{2-}$ used in this reaction is not recovered, since $Z \neq H_2O$, but forms *trans*-$PtCl_2(H_2O)_2$. However, since $PtCl_4^{2-}$ is always present in large excess relative to platinum(IV) complex, its concentration can be regarded as constant during the reaction.

34 L.I. Elding and L. Gustafson, to be published.

35 L.I. Elding and L. Gustafson, to be published.

36 V.I. Kravtsov and L.Y. Smirnova, *Elektrokhimiya, 6,* 1813 (1970).