On the Stepwise Dissociation of the Tetrachlorido-platinate(II) Ion in Aqueous Solution

I. Equilibria at 25°C

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Dissociation constants of the first and second aquation reactions of the tetrachloridoplatinate(II) ion have been determined from spectrophotometric measurements at 230 and 315 nm. The constant of the second dissociation has also been calculated from separations of negatively charged complexes from uncharged ones with the help of an anion exchanger.

The solutions were aged for 3—4 weeks. The ionic medium was 0.500 M $HClO_4$ and the temperature 25.0°C. The constants calculated have been collected in Table 1.
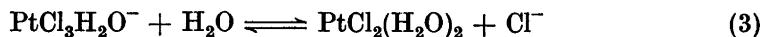
Both the kinetics and the equilibrium of the aquation reaction

$$PtCl_4{}^{2-} + H_2O \rightleftharpoons PtCl_3H_2O^- + Cl^- \tag{1}$$

have been studied by a few authors during the last decade (Table 1). The dissociation constant, K_4, is defined by

$$K_4 = \frac{[PtCl_3{}^-]\ [Cl^-]}{[PtCl_4{}^{2-}]} \tag{2}$$

For the dissociation constant K_3 for the following dissociation step

$$PtCl_3H_2O^- + H_2O \rightleftharpoons PtCl_2(H_2O)_2 + Cl^- \tag{3}$$

we have found only one preliminary value in the relevant literature (Table 1).

$$K_3 = \frac{[PtCl_2]\ [Cl^-]}{[PtCl_3{}^-]} \tag{4}$$

In eqn. (4) $[PtCl_2]$ stands for the sum of the concentrations at equilibrium of the *cis*- and *trans*-isomers of $PtCl_2(H_2O)_2$.

In this paper K_4 and K_3 have been calculated from spectrophotometric measurements and K_3 also from anion exchange measurements. In a paper which will be published later (Ref. 4) an independent determination of the rate constants for both the forward reaction and the reverse one in (1) will be described. The quotient of these two rate constants agrees satisfactorily with our result for K_4 given here (*vide* Table 1).

We have also tried to determine the concentration of free chloride ions in aged solutions of K_2PtCl_4 with the help of silver-silver chloride electrodes, in the same way as Leden and Chatt [5] used such electrodes in solutions of Zeise's salt. But the drift of the potential because of side reactions was too fast in the present case for this method to be used.

Table 1. Survey of determinations of the dissociation constants K_4 (M) and K_3 (M).

Author	Ref.	Method	Temp °C	Ionic strength M	$K_4 \times 10^3$	$K_3 \times 10^3$
Martin *et al.*	1	Titr. with OH⁻	25	0.318	18	—
Sanders, Martin	2	»	25	0.318	15 ± 2	0.5 ± 0.3
» »	2	»	25	0	30 ± 15	1.0 ± 0.6
Grinberg, Shagisultanova	3	»	17—18	0.1	18	—
This paper		Anion exch.	25	0.500	—	1.0 ± 0.1
» »		Spectr.	25	0.500	13.₄ ± 1	1.1 ± 0.1
Elding	4	Kinetics	25	0.500	13 ± 1	—

EXPERIMENTAL

Chemicals. Potassium tetrachloridoplatinate(II) (Degussa) was used without further purification. Unlike preparations from some other firms its spectrum, in 0.5 M hydrochloric acid, did not change after recrystallisation from hydrochloric acid. It contained less than 0.5 % Pt(IV) as was judged from the spectrum at 262 nm, where the molar absorptivity of $PtCl_4{}^{2-}$ is low and the spectrum of $PtCl_6{}^{2-}$ has a strong maximum, $\varepsilon_{max} = 2.5 \times 10^4$ (cm⁻¹ M⁻¹). The salt was analysed for platinum by reduction to metal with hydrazine sulphate in sodium hydrocarbonate solution. The platinum was filtered away and weighed and the chloride contents of the filtrate determined by a differential potentiometric titration (Güntelberg [6, p. 85]). Result: Pt 46.6 %, Cl 33.9 %. Calc. for K_2PtCl_4: Pt 47.00 %, Cl 34.16 %.

Perchloric acid (Baker's *p.a.*) and hydrochloric acid (Merck's *p.a.*) were used to prepare stock solutions.

Ion exchangers. The cation exchanger (Dowex 50 W × 8, 50—100 mesh) in H⁺-form was washed thoroughly with water. The anion exchanger (Dowex 1 × 4, 50—100 mesh) was washed with hydrochloric acid until the eluate was no longer yellow, and then brought into its perchlorate form with 3 M perchloric acid.

Equipment. Spectra were obtained by a Beckman Recording Spectrophotometer, Model DK 1. Measurements at constant wavelength were performed by a Beckman Quartz Spectrophotometer, Model DU.

The solutions were aged in thermostats at 25.0 ± 0.1°C.

The matched cells were of Hellma's Quartz Suprasil quality. The following path lengths were used: 5.001, 2.001, 1.000, 0.500, 0.200, 0.1000, 0.0512, 0.01907, and 0.00959 cm.

ION EXCHANGE MEASUREMENTS

Because of the slow reactions of the complexes ion exchangers can be used to separate charged species from uncharged ones or species of opposite charge from each other in an aged solution in which equilibrium between such species has been established.

Cation exchange experiments. If an equilibrated solution contains a cation, *e.g.* $PtCl^+$, platinum should be retained by a cation exchanger. Even from those solutions, which contained the smallest concentrations of chloride ion ($< 10^{-3}$ M) no platinum was taken up by an exchanger, saturated with hydrogen ions. When aged solutions were percolated through such an exchanger, all the platinum was always refound in the eluate, when the resin was washed with water. Neither could any platinum be eluted from the washed resin, when perchloric acid was percolated through it.

From this we conclude that none of our solutions contained as much as 5 % of the platinum in cationic complexes. This means that most of our solutions can contain only negligible concentrations of platinum in cations. The method for determination of platinum was the same as described below.

Anion exchange experiments. The columns used were 50 cm long with an inner diameter of 1.2 cm. The flow rate was 3 ml/min. Grinberg[7] and Martin[2] report that some reduction occurs when solutions of platinum(II)-salts are percolated through an exchanger. No such reduction was found, however, in this investigation, if the experiments were carried out with acidic solutions in the dark. It was always possible to recover the platinum ($PtCl_4^{2-}$ + $PtCl_3^-$) quantitatively from the resin by elution with perchloric acid.

Five solutions were used for the experiments. They were produced by dissolving potassium tetrachloridoplatinate(II) in 0.5 M $HClO_4$. The concentrations of platinum were 0.5, 1, 2, 3, and 5 mM, respectively. The solutions were aged for 3—4 weeks at 25°C. Different volumes (3—50 ml) were percolated through the column, which was then washed with 200—500 ml of water. The eluate, containing the uncharged $PtCl_2$ present in the equilibrated solution, was collected in a volumetric flask and analysed for platinum. The percolation of the platinum solution through the ion exchanger required 10—20 min. During this time only a negligible conversion of $PtCl_2$ to $PtCl_3^-$ will occur according to our kinetic measurements.

Analyses. The platinum of the eluates was analysed spectrophotometrically as $PtCl_4^{2-}$. 25 ml of the eluate and 25 ml of 6 M HCl were mixed. Within a few hours practically all platinum was converted into $PtCl_4^{2-}$. The solutions were allowed to stand for 24 h at 25°C. Then their absorbance was measured at 230 and 217 nm. The reference cell was filled with a mixture of 25 ml of water percolated through the column and 25 ml of 6 M HCl. Thus the concentration of platinum could be calculated at the two wavelengths by a comparison with solutions containing known concentrations of $PtCl_4^{2-}$ in the same medium. The mean value of the analyses was used to calculate the percentage of $PtCl_2(H_2O)_2$. The method allows determination of platinum down to 1 μmole or 10 μM with an accuracy better than 5 %. In order to control that no oxidation to Pt(IV) occurred in the solutions, the absorbance was also measured at the strong maximum of $PtCl_6^{2-}$ at 262 nm. No such oxidation could be observed.

Table 2. Determination of % of platinum as $PtCl_2(H_2O)_2$ by anion exchange experiments. Each percentage is the mean of at least four experiments with different volumes. All results obtained lie within the given limits. C_{Pt} and K_3 in M.

$C_{Pt} \times 10^3$	% $PtCl_2(H_2O)_2$	$K_3 \times 10^3$
5.00	15.0 ± 0.4	1.11
3.02	19.8 ± 0.5	0.97
2.010	26.6 ± 0.5	0.98
1.000	40 ± 1	0.98
0.500	53 ± 2	0.90
		Mean 1.0 ± 0.1

Results. The solutions used contained only small amounts of $PtCl_4^{2-}$ at equilibrium (22 % in the 5 mM solution, less in the others). The method was thus designed to measure K_3. Table 2 reviews the measurements. K_3 was calculated from eqns. (2), (4) and the stoichiometric conditions (5) and (6), in which C_{Pt}, $[PtCl_2]$ and K_4 are known.

$$C_{Pt} = \sum_{i=2}^{4} [PtCl_i^{2-i}] \tag{5}$$

$$[Cl^-] = [PtCl_3(H_2O)^-] + 2[PtCl_2(H_2O)_2] \tag{6}$$

The spectrophotometric value of $K_4 = 13.4 \times 10^{-3}$ (M) was used. The computed K_3 is insensible to the used value of K_4. If K_4 is varied 25 %, this causes a shift in K_3 of only 2 % (for the 5 mM solution, less for the others).

SPECTROPHOTOMETRIC MEASUREMENTS

The method of corresponding solutions (Bjerrum,[8] Olerup,[9,10] Fronæus[11]) has been used. In our case this method works as follows. Let us define the function X as

$$X = 1 + K_3^{-1} [Cl^-] + K_3^{-1} K_4^{-1} [Cl^-]^2 \tag{7}$$

Then eqn. (5) can be rewritten as

$$C_{Pt} = [PtCl_2] \cdot X \tag{8}$$

Since cationic platinum species can be neglected in this case the average number, $\bar{n}$, of chloride ligands bound per platinum atom, defined as

$$\bar{n} = (C_{Cl} - [Cl^-])/C_{Pt}, \text{ or } C_{Cl} = \bar{n} \cdot C_{Pt} + [Cl^-] \tag{9}$$

becomes

$$\bar{n} = \frac{\sum_{i=2}^{4} i \, [PtCl_i^{2-i}]}{\sum_{i=2}^{4} [PtCl_i^{2-i}]} \tag{10}$$

Eqns. (7), (8), and (10) give

$$\bar{n} - 2 = \frac{X'[\text{Cl}^-]}{X} \tag{11}$$

where $X' = \dfrac{\mathrm{d}X}{\mathrm{d}[\text{Cl}^-]}$ $\qquad\qquad$ (12)

By integrating eqn. (11) between a fixed limit $[\text{Cl}^-]_0$ and a varied limit $[\text{Cl}^-]_j$, we get the result

$$\ln X_j - \ln X_0 = \int_{[\text{Cl}^-]_0}^{[\text{Cl}^-]_j} \frac{\bar{n}-2}{[\text{Cl}^-]} \, \mathrm{d}[\text{Cl}^-] \tag{13}$$

from which X_j may be determined at selected $[\text{Cl}^-]_j$ by a graphic integration, if we can determine $\bar{n}$ as a function of $[\text{Cl}^-]$. Spectrophotometric measurements give us immediately this last connection. Let e be the absorptivity, *i.e.* absorbance per unit path length, and ε_i the molar absorptivity of PtCl_i^{2-i} at a fixed wavelength.
Then

$$e = \sum_{i=2}^{4} \varepsilon_i \, [\text{PtCl}_i^{2-i}] \tag{14}$$

since the absorbance of chloride ions is negligible in our range of measurements. The absorptivity per M of platinum present in the solution, ε_{Pt}, is then

$$\varepsilon_{\text{Pt}} = e / C_{\text{Pt}} \tag{15}$$

which gives, together with eqns. (7), (8), and (14)

$$\varepsilon_{\text{Pt}} = \frac{\varepsilon_2 + \varepsilon_3 \, K_3^{-1} \, [\text{Cl}^-] + \varepsilon_4 \, K_3^{-1} \, K_4^{-1} \, [\text{Cl}^-]^2}{X} \tag{16}$$

Hence, at a given wavelength, ε_{Pt} is a function of $[\text{Cl}^-]$ only.
ε_{Pt} has been determined at a constant C_{Pt} and varied C_{Cl}. This series of experiments has then been repeated for a few other values of C_{Pt} giving a family of curves, one curve for each C_{Pt} (see Fig. 2).
If these curves are cut by a straight line parallel to the C_{Cl}-axis, the points of intersection obviously point out solutions containing equal concentrations of free chloride ions, since ε_{Pt} is the same for all these solutions. Because $\bar{n}$ is also a function of $[\text{Cl}^-]$ only (eqn. 11), eqn. (9) tells us that C_{Cl}, drawn as a function of C_{Pt} for the points of intersection, should give us a straight line of slope $\bar{n}$ and origo ordinate $[\text{Cl}^-]$.
By drawing lines at other values of ε_{Pt} in diagrams like Fig. 2, we get a set of corresponding values of $\bar{n}$ and $[\text{Cl}^-]$ from which X is then determined as a function of $[\text{Cl}^-]$ in the manner outlined above.
Finally, K_3 and K_4 are obtained, *e.g.* from a graph of $X_1 = (X-1)[\text{Cl}^-]^{-1}$ as a function of $[\text{Cl}^-]$, which should be a straight line, *viz.*

$$X_1 = (X-1) \, [\text{Cl}^-]^{-1} = K_3^{-1} + K_3^{-1} \, K_4^{-1} \, [\text{Cl}^-] \tag{17}$$

Results. Some spectra of aged solutions at varied chloride concentrations are shown in Fig. 1. The formation of the neutral complex in solutions with a concentration of free chloride smaller than about 7 mM is demonstrated by the deviation of spectra 4 and 5 from the isosbestic points.
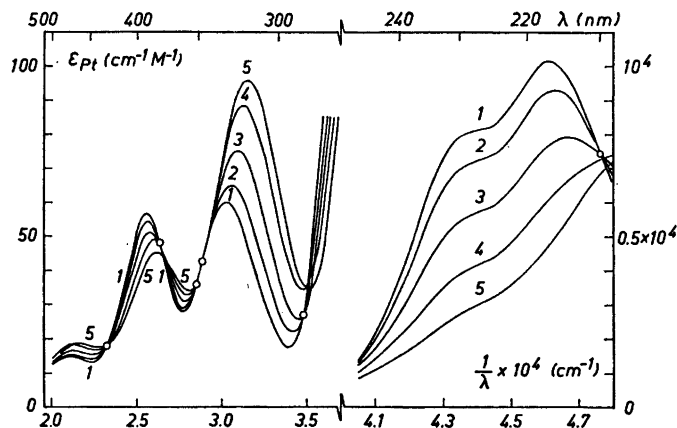

Fig. 1. Absorption spectra of aged solutions. $C_{Pt} = 1.000$ (mM). C_{Cl} was varied: 1, 504; 2, 54.0; 3, 20.00; 4, 10.00; 5, 6.00 (mM). Solution 1 contains 97.5 % of its Pt in $PtCl_4^{2-}$. Isosbestic points ($\varepsilon_4 = \varepsilon_3$) have been marked with O.

Table 3. Spectrophotometric measurements at 315 nm. C_{Pt} and C_{Cl} in M, ε_{Pt} in $cm^{-1}M^{-1}$.

$C_{Pt} \times 10^3$	$C_{Cl} \times 10^3$	ε_{Pt}	$C_{Pt} \times 10^3$	$C_{Cl} \times 10^3$	ε_{Pt}
25.00	100.0	76.1	1.000	4.00	102.0
23.15	92.6	76.7	1.000	5.00	100.0
20.00	80.0	77.9	1.000	6.00	97.2
17.86	71.4	79.4	1.000	7.00	94.8
15.00	60.0	81.2	1.000	8.00	93.2
15.00	62.0	79.1	1.000	9.00	90.6
15.00	66.0	75.1	1.000	10.00	89.6
15.00	70.0	71.7	1.000	11.00	87.4
15.00	80.0	65.5	1.000	12.00	83.6
13.89	55.6	82.1	1.000	14.00	79.8
10.00	40.0	85.5	1.000	16.00	76.8
10.00	42.0	82.6	1.000	18.00	74.2
10.00	46.0	77.6	1.000	20.00	72.4
10.00	50.0	73.6	1.000	22.00	70.6
10.00	54.0	69.9	1.000	24.00	68.8
10.00	60.0	66.4	1.000	29.00	65.6
10.00	70.0	61.8	1.000	34.0	62.8
7.50	30.0	89.1	1.000	39.0	61.0
5.00	20.00	93.2	1.000	44.0	59.6
4.00	16.00	95.5	1.000	54.0	57.0

Table 4. Corresponding values of $[Cl^-]$ (M), $\bar{n}$ and $(\bar{n}-2)/[Cl^-]$ (M^{-1}) at a number of selected ε_{Pt} $(cm^{-1}M^{-1})$.

ε_{Pt}	$[Cl^-] \times 10^3$	$\bar{n}$	$\dfrac{\bar{n}-2}{[Cl^-]} \times 10^{-1}$
	From measurements at 230 nm.		
5970	25.2	3.65	6.6
5650	20.8	3.55	7.5
5385	17.1	3.53	9.0
5040	13.8	3.49	10.8
4800	12.2	3.45	11.9
4670	11.4	3.42	12.5
4350	9.3	3.38	14.8
4210	8.8	3.32	15.0
3930	7.3	3.26	17.3
3590	6.1	3.17	19.2
3380	5.4	3.12	20.7
3210	4.8	3.05	21.9
2775	3.5$_1$	3.00	28.5
2435	2.7$_0$	2.88	32.$_6$
2190	2.1$_8$	2.77	35.$_3$
1790	1.4$_2$	2.66	46.$_5$
	From measurements at 315 nm.		
61.8	33.2	3.68	5.1
64.0	28.1	3.66	5.9
65.5	25.7	3.62	6.3
67.5	22.5	3.58	7.0
69.0	20.3	3.56	7.7
71.7	17.2	3.50	8.7
74.0	14.8	3.49	10.1
76.1	13.0	3.46	11.2
78.0	11.7	3.42	12.1
81.2	9.9	3.34	13.5
85.5	7.8	3.22	15.6
89.1	6.3	3.16	18.4
93.2	4.7	3.06	22.6
95.5	3.9	3.02	26.1

The dissociation constants K_4 and K_3 have been calculated from measurements at 230 and 315 nm. Fig. 2 reviews the measurements at 230 nm, and in Table 3 we have collected the measurements at 315 nm. From this table, a diagram similar to Fig. 2 may be constructed. In Table 4 the corresponding values of $\bar{n}$ and $[Cl^-]$ obtained by cutting the ε_{Pt}, C_{Cl}-curves at a number of selected ε_{Pt} have been introduced.

X has been computed by a graphic integration of $(\bar{n}-2)[Cl^-]^{-1}$ *vs.* $[Cl^-]$ (Fig. 3). This curve has a very steep slope near the ordinate axis because of the strong complexity. As the lower integration limit, $[Cl^-]_0$, 2×10^{-3} M was chosen. According to (13) the integration then gives $X/X(2)$. The constant $1/X(2)$ was determined as 0.32 ± 0.03 by extrapolation to zero chloride concentration of the function $X/X(2)$. Then X and X_1 could be calculated (*vide* Table 5).

Table 5. The calculation of X and X_1. The values of $X/X(2)$ and X_1 at zero chloride concentration were obtained by extrapolation. [Cl⁻] in M, X_1 in M⁻¹.

[Cl⁻] × 10³	ln $\dfrac{X}{X(2)}$	$\dfrac{X}{X(2)}$	X	$X_1 \times 10^{-3}$
0		0.32		0.92
2	0	1.00	3.13	1.07
3	0.3393	1.40	4.39	1.13
4	0.6110	1.84	5.76	1.19
5	0.8423	2.32	7.25	1.25
6	1.0463	2.85	8.89	1.32
7	1.2300	3.42	10.69	1.38
8	1.3970	4.04	12.63	1.45
10	1.6920	5.42	16.94	1.59
12	1.9468	7.00	21.9	1.74
14	2.1712	8.77	27.4	1.89
16	2.3707	10.71	33.5	2.03
18	2.5499	12.80	40.0	2.17
20	2.7122	15.06	47.1	2.31
22	2.8614	17.48	54.6	2.44
24	2.9998	20.1	62.7	2.57
26	3.1286	22.8	71.3	2.70
28	3.2498	25.8	80.5	2.84

Fig. 4 shows the plot of X_1 *vs.* [Cl⁻] from which K_3 and K_4 were obtained according to (17):

$$K_4 = (13._4 \pm 1) \times 10^{-3} \text{ (M)}$$
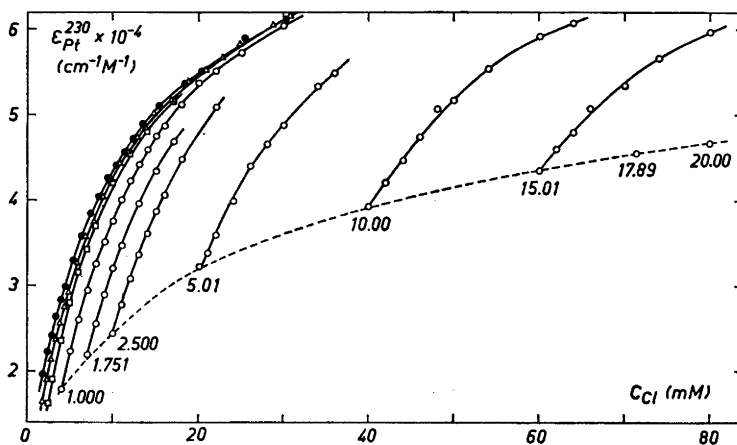$$K_3 = (1.1 \pm 0.1) \times 10^{-3} \text{ (M)}$$

Fig. 2. Measurements at 230 nm. ε_{Pt} as a function of C_{Cl} at different C_{Pt} (C_{Pt} in mM). The dashed curve represents solutions with $C\bar{C}l = 4 \times C_{Pt}$, *i.e.* no extra chloride has been added to these solutions. C_{Pt}: □, 0.500; △, 0.2014; ●, 0.1000 (mM).

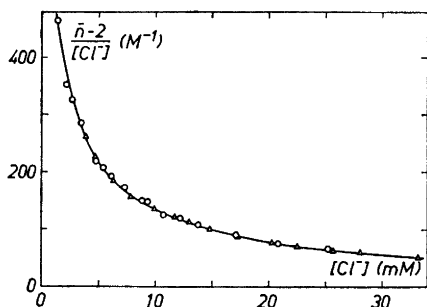*Fig. 3.* $(\bar{n}-2)/[Cl^-]$ as a function of $[Cl^-]$, the integration of which gives $\ln(X/X(2))$, if $[Cl^-] = 2$ is chosen as the lower integration limit. $\triangle$, 315; $\bigcirc$, 230 nm.
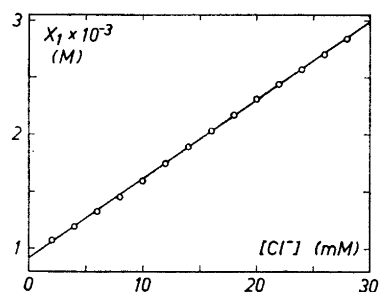
Fig. 4. X_1 as a function of $[Cl^-]$. The origo ordinate gives $K_3^{-1} = 920$ (M^{-1}) and the slope $K_3^{-1}K_4^{-1} = 68.7 \times 10^3$ (M^{-2}).

In Fig. 5a, $\bar{n}$, calculated from the two constants by means of (7), (11) and (12), has been drawn as a function of log $[Cl^-]$. The function may be compared to the $\bar{n}$, log $[Cl^-]$-values calculated from the experiments. The measurements at the two wavelengths agree within the experimental uncertainties.

In Fig. 5b, the distribution of platinum between the different complexes as a function of log $[Cl^-]$ has been calculated.
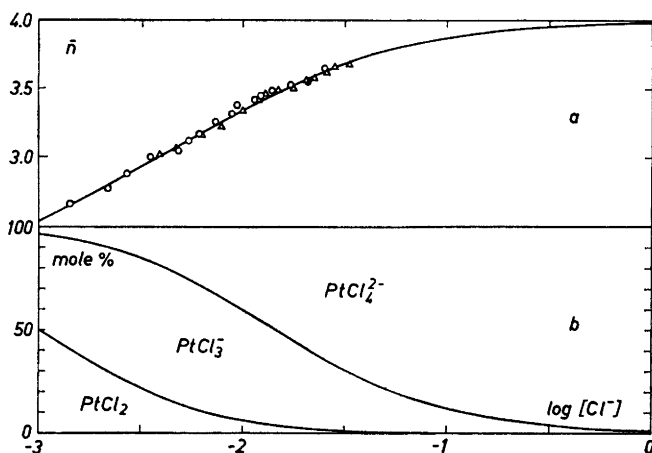

Fig. 5. a. The function $\bar{n}(\log [Cl^-])$ from measurements at the two wavelengths ($\triangle$, 315; $\bigcirc$, 230 nm) compared to the formation curve calculated from K_3 and K_4. b. The distribution of platinum between different complexes in aged solutions as a function of log $[Cl^-]$. $[Cl^-]$ in M.

CONCLUSIONS

Previous investigations (Table 1, Refs. 1, 3) give a value of K_4 which is considerably higher than the one calculated here. However, in these investigations, the second dissociation was neglected. This will result in too high a value of the constant, even if the percentage of $PtCl_2$ at equilibrium is not greater than $5-10$ %.

In the present investigation it is presupposed that equilibrium between the two isomers of $PtCl_2(H_2O)_2$ and the other complexes has been established. Present kinetic experiments indicate that the *trans*-isomer is formed rather slowly. However, an aging time of 3 to 4 weeks seems to be sufficiently long, so that the *trans*-isomer ought to be at least near the equilibrium with the other species. Then $[PtCl_2]$ in (4) will represent the sum of the concentrations of the two isomers. Perhaps the low value of Sanders and Martin,[2] calculated with an aging time of 1 to 3 days only, may represent a constant K_{3cis}, defined analogously to (4), rather than K_3. In their case $[PtCl_2]$ would then mean the concentration of the *cis*-isomer exclusively.

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