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

IV. The Chlorotriaquaplatinum(II) Ion

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Solutions of K_2PtCl_4 ($10^{-3}-10^{-4}$ M) were aged at 60.0°C in an aqueous perchloric acid medium of ionic strength 0.50 M. At equilibrium, these solutions contain up to 40 % of the platinum as $PtCl(H_2O)_3{}^+$. This species was separated from the other complexes of the equilibrium mixture and its concentration determined using cation exchange columns. It is so stable that measurable amounts of the tetraaqua ion $Pt(H_2O)_4{}^{2+}$ do not form in the range of concentration available.

The dissociation constants K_n, eqn. (1), for the substitution of one chloride ligand by water in the complexes $PtCl_n(H_2O)_{4-n}{}^{2-n}$, $n=2$, 3, 4, were calculated at 60.0 and 25.0°C from spectrophotometric measurements using a least squares method (Table 3). The enthalpy changes were also obtained: $\Delta H_4=3\pm1$, $\Delta H_3=2\pm1$ and $\Delta H_2>0$ (kcal mol^{-1}). Estimated stability constants for the platinum(II)-chloro complexes at 60.0 and 25.0°C are given in Table 5.

The chloro-aqua complexes $PtCl_3H_2O^-$ and $PtCl_2(H_2O)_2$ have been shown [1,2] to exist in aqueous solutions of K_2PtCl_4, aged at 25°C. They are formed by stepwise substitutions of the chloride ligands by water in the tetrachloroplatinate(II)-ion. Kinetic measurements presented in subsequent papers [3,4] indicate that $PtCl_2(H_2O)_2$ may be present both as a *cis*- and a *trans*- isomer in aqueous solution. The equilibrium constants K_4 and K_3, defined by eqn. (1), have been determined.[1,2]

$$K_n = [PtCl_{n-1}(H_2O)_{5-n}^{3-n}]\cdot[Cl^-]\cdot[PtCl_n(H_2O)_{4-n}^{2-n}]^{-1};\ n = 1, 2, 3, 4 \qquad (1)$$

The aim of the present study was to investigate the formation of cationic complexes by the acid hydrolysis [5] of $PtCl_2(H_2O)_2$.

The equilibrium concentrations of cationic species will increase in solutions aged at elevated temperatures. An increase of temperature will also accelerate the rates of acid hydrolysis of the complexes by a factor of 2 – 3 for each 10 degrees. This will reduce the time necessary to reach equilibrium from about 1800 h at 25°C to about 60 h at 60°C (the rate determining acid hydrolysis reaction of the system has a half-life of about 270 h at 25°C [4]).

Solutions of K_2PtCl_4 have been equilibrated at 60°C and then rapidly chilled to 25°C or about 0°C for spectrophotometric or cation exchange analysis. This procedure will only cause a negligible displacement of the position of the equilibrium at 60°C, since the complex equilibria are established very slowly at room temperature.

The cationic complex formed in these solutions, $PtCl(H_2O)_3^+$, has been separated quantitatively from the neutral and anionic species of the equilibrium mixture by percolating the chilled solutions through cation exchange columns. These separations give a value of the equilibrium constant K_2 of eqn. (1). The spectrophotometric measurements are also consistent with the formation of one cationic complex and give the equilibrium constants K_4, K_3, and K_2 of eqn. (1).

The tetraaquaplatinum(II)-ion $Pt(H_2O)_4^{2+}$ could not be detected, since the chloro complexes are too stable. Attempts to produce this species in measurable concentration by some other methods than equilibrating dilute solutions of K_2PtCl_4 at elevated temperatures will be discussed in the final part of the paper.*

SPECTROPHOTOMETRIC MEASUREMENTS

Experimental

Chemicals and apparatus, cf. Ref. 6.

Measurements. Series of solutions of K_2PtCl_4, each with a constant concentration of platinum, C_{Pt}, and varying total concentrations of chloride, C_{Cl}, were prepared (Table 1). C_{Cl} is given by $C_{Cl}=4\times C_{Pt}+[Cl^-]_0$, where $[Cl^-]_0$ is the concentration of extra chloride added to the solutions as HCl. The ionic medium was $HClO_4$ and the ionic strength 0.50 M. The solutions were aged at (60.0 ± 0.1)°C for 3–7 days. Kinetic experiments [4] indicate that equilibrium at 60°C is established within 3 days. The solutions were rapidly chilled to about 25°C by pouring them into Erlenmeyer flasks in an ice-bath. The absorbance was immediately measured at 315 or 230 nm. The equilibrium concentrations at 60°C will not change appreciably during the short time (1–2 min) needed for cooling and measurement.

The half-life for the reaction between chloride and $PtCl^+$, for instance, is about 20–30 min at 25°C at the pertinent concentrations of free chloride ($<10^{-3}$ M).[3]

Calculations and results

The results of the experiments are given in Fig. 1. The method of corresponding solutions, described in Ref. 2 and papers cited therein, gave the dissociation constants K_4 and K_3 of Table 3. The values of $\bar{n}(\log[Cl^-])$ calculated by this method are given in Fig. 2 a.

The most dilute solutions, which will be the most interesting ones when looking for a further dissociation to cationic complexes, cannot be utilized in this method of calculation. Since always $C_{Cl}\geqslant 4\times C_{Pt}$ for these solutions

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

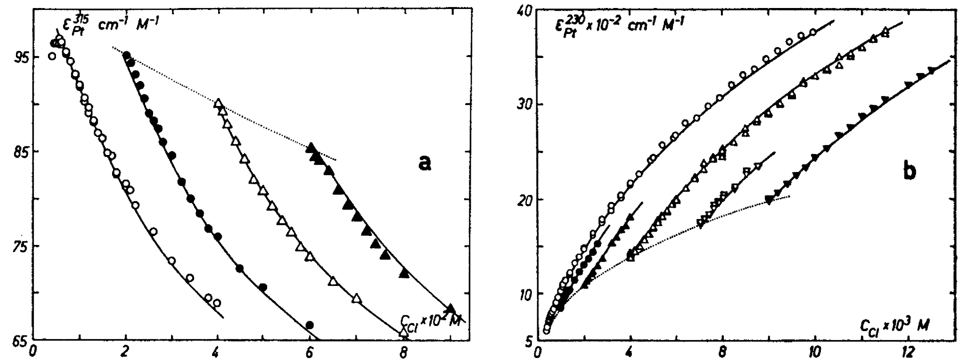

Fig. 1. a. Measurements at 315 nm. $\varepsilon_{\mathrm{Pt}}$ as a function of C_{Cl} at the following concentrations of platinum in mM; 15.00 ▲, 10.00 △, 5.00 ● and 0.979 ○.
b. Measurements at 230 nm. $\varepsilon_{\mathrm{Pt}}$ as a function of C_{Cl} at the following concentrations of platinum in mM: 2.500 ▼, 1.763 ▽, 1.003 △, 0.501 ▲, 0.2503 ● and 0.1003 ○. The full-drawn curves are calculated by the computer from the values of K_n and ε_n obtained by the least squares method (Table 2); the dotted curves represent solutions having $C_{\mathrm{Cl}} = 4 \times C_{\mathrm{Pt}}$.

of K_2PtCl_4, the $\varepsilon_{\mathrm{Pt}}$, C_{Cl}-curves for each value of C_{Pt} cannot be extended beyond the dotted curves of Fig. 1. Therefore, for low values of the mean ligand number $\bar{n}$, the curves available come too close to each other to permit accurate determination of $\bar{n}$. The lowest value of $\bar{n}$ calculated was about 2.5, corresponding to $\varepsilon_{\mathrm{Pt}}^{230} = 1400$ (cm^{-1}M^{-1}) (*cf.* Fig. 1 b). The calculations from the measurements at 315 nm become less exact also, since $\varepsilon_{\mathrm{Pt}}^{315}$ only changes from about 70 to 90 cm^{-1}M^{-1} in the interval used at this wavelength (*cf.* Fig. 1 a).

The least squares program "Letagrop Spek" developed by Sillén and Warnqvist[7] is more suitable for calculation in this case. The input data, given in Table 1, were the total concentrations C_{Pt} and C_{Cl} and the molar absorptivity $\varepsilon_{\mathrm{Pt}}$ of each solution. The error square sum to be minimized was

$$U_{\mathrm{rel}} = \sum_i (\varepsilon_{\mathrm{Pt},i,\mathrm{calc}} - \varepsilon_{\mathrm{Pt},i,\mathrm{exp}})^2 \cdot \varepsilon_{\mathrm{Pt},i,\mathrm{exp}}^{-2} \qquad (2)$$

The calculation gives the stability constants, β_n, and the molar absorptivities, ε_n, of the complex species. The molar absorptivity of $PtCl_4^{2-}$, ε_4, was determined separately.

The results are given in Table 2. The experiments may be described either by a model including the four complexes $PtCl_4^{2-}$, $PtCl_3^-$, $PtCl_2$ and $PtCl^+$ (columns 1 – 3) or by a model which only includes the three first-mentioned of these species (column 4). It appears from Table 2 that the values of U_{rel} and *sigy* obtained for these two models do not differ significantly. The good fit obtained for the calculation given in column 4 is made possible by a relatively big change of the molar absorptivities (ε_2^{230} decreases 25 %). Since the cation exchange measurements (*vide infra*) indicate the formation of the complex $PtCl^+$ in these solutions, the first-mentioned model is obviously the correct one. It was used for the interpretation of the measurements.

Table 1. Experimental values of $C_{\mathrm{Cl}} \times 10^3$ M, $\varepsilon_{\mathrm{Pt}}$ cm^{-1}M^{-1} at different values of $C_{\mathrm{Pt}} \times 10^3$ M (printed in italics) at 315 and 230 nm.

	315 nm									
0.979:	3.92,	95.1;	4.42,	96.5;	4.92,	96.5;	5.42,	96.8;	5.92,	96.5;
	6.92,	95.5;	7.92,	94.6;	8.92,	93.2;	9.92,	92.0;	10.92,	90.5;
	11.92,	89.4;	12.92,	88.3;	13.92,	87.0;	14.92,	86.4;	15.92,	84.9;
	16.92,	84.6;	17.92,	82.7;	19.92,	81.5;	20.92,	80.9;	21.92,	79.3;
	25.92.	76.5;	29.92,	73.4;	33.9,	71.6;	37.9,	69.5;	39.9,	68.9;
5.00:	20.00,	95.2;	21.00,	94.4;	22.00	93.2;	23.00,	92.0;	24.00,	90.6;
	25.00,	89.0;	26.00.	88.2;	27.00,	87.4:	28.00,	86.0;	30.0,	84.6;
	32.0,	81.8;	34.0,	80.0;	36.0,	78.4;	38.0,	76.8;	40.0,	76.0;
	45.0,	72.6;	50.0,	70.6;	60.0,	66.6;				
10.00:	40.0,	89.0;	41.0,	89.2;	42.0,	87.8;	44.0,	86.0;	46.0,	84.2;
	48.0,	82.0;	50.0,	80.8;	52.0,	79.2;	54.0,	77.6;	56.0,	76.4;
	58.0,	74.8;	60.0,	73.8;	65.0,	71.2;	70.0,	69.4;	80.0,	65.8;
15.00:	60.0,	85.3;	61.0,	84.4;	62.0,	84.0;	64.0,	82.9;	66.0,	80.8;
	68.0,	79.3,	70.0,	78.0;	72.0,	76.5;	74.0,	75.2;	76.0,	74.0;
	80.0,	72.0;	90.0,	68.3;						
25.00:	100.0,	82.2;								
	230 nm									
0.1000:	0.400,	610;	0.450,	676;	0.500,	702;	0.550,	742;	0.600,	775;
	0.650,	806;	0.700,	834;	0.750,	860;	0.800.	897;	0.900,	952;
	1.000,	1024;	1.100,	1072;	1.200,	1134;	1.400,	1219;	1.800,	1380;
	2.000,	1464;	2.400,	1618;	2.800,	1783;	3.20,	1923;	3.60,	2038;
	4.00,	2163;	4.90,	2410;	5.00,	2438;	5.40,	2570;	5.90,	2645;
	6.00,	2677;	6.40,	2805;	6.90,	2855;	7.40,	2980;	7.90,	3070;
	8.40,	3205;	8.90,	3310;	9.40,	3370;	9.90,	3475;	10.40,	3560;
	10.90,	3655;	11.40,	3720;	11.90,	3755;				
0.1006:	0.402,	634;	0.502,	729;	0.602,	783;	0.702,	839;	0.802,	904;
	0.902,	956;	1.102,	1097;	1.402,	1209;	1.602,	1318;	1.802,	1381;
	2.002,	1480;	2.402,	1634;	2.802,	1744;	3.20,	1878;	3.60,	2006;
	4.00,	2151;	4.40,	2260;						
0.2503:	1.001,	832;	1.101,	910;	1.201,	972;	1.301,	1008;	1.401,	1038;
	1.501,	1119;	1.601,	1139;	1.701.	1195;	1.801,	1224;	2.001,	1299;
	2.201,	1365;	2.401,	1433;	2.601,	1527;				
0.501:	2.000,	1074;	2.100,	1114;	2.200,	1142;	2.300,	1194;	2.400,	1228;
	2.600,	1283;	2.800,	1363;	3.20,	1529;	3.40,	1589;	3.60,	1665;
	3.80,	1709;	4.00,	1804;						
0.979:	3.92,	1372;	4.42,	1525;	4.92,	1682;	5.42,	1835;	5.92,	1982;
	6.92,	2247;	7.92,	2503;	8.92,	2748;	9.92,	2952;	10.92,	3146;
	11.92,	3320;	12.92,	3476;	13.92,	3633;				
1.001:	4.00,	1406;	4.20,	1456;	4.60,	1568;	4.80,	1617;	5.00,	1697;
	5.20,	1776;	5.40,	1821;	5.60,	1871;	5.80,	1935;	6.00,	2005;
	6.40,	2109;	6.80,	2204;	7.20,	2313;	7.60,	2413;	8.00,	2477;
	8.50,	2587;	9.00,	2714;	9.50,	2823;	10.00,	2900;	10.50,	2992;
	11.00,	3093;	11.50,	3229;	12.00,	3283;	12.50,	3359;	13.00,	3447;
	13.50,	3512;	14.00,	3587;	14.50,	3680;	15.00,	3755;		
1.006:	4.02,	1366;	4.22,	1427;	4.42,	1487;	4.62,	1559;	4.82,	1612;
	5.02,	1681;	5.22,	1741;	5.42,	1810;	5.62,	1864;	5.82,	1948;
	6.02,	1983;	6.42,	2107;	6.82,	2225;	7.22,	2379;	7.62,	2438;
	8.02,	2532;								
1.763:	7.05,	1739;	7.25,	1793;	7.45,	1835;	7.65,	1920;	7.85,	1963;
	8.05,	2037;	8.55,	2138;	9.05,	2283;	9.55,	2354;		
2.500:	10.00,	1989;	10.40;	2068;	10.80,	2160;	11.20,	2256;	11.60,	2332;
	12.00,	2440;	12.50,	2536;	13.00,	2672;	13.50,	2756;	14.00,	2872;
	14.50,	2956;	15.00,	3048;	16.00,	3204;	16.50,	3296;	17.00,	3356;

Table 2. Calculations of the dissociation constants K_4, K_3, and K_2 M of eqn. (1), using the least squares program Letagrop Spek.[7] Parameters printed in italics were not varied. The stability constants, β_n, are given in M^{-n}, the molar absorptivities, ε_n, in $cm^{-1}M^{-1}$. $\varepsilon_4^{315}=43.4$ and $\varepsilon_4^{230}=8020$ were given as constants in the calculations. The errors are given as 1σ. *sigy* is the standard deviation for the relative differences between experimental and calculated ε_{Pt}. The error square sum, U_{rel}, is defined by eqn. (2).

Run Constant	1	2	3	4
$\beta_4 \times 10^{-12}$	9.16 ± 0.37	9.51 ± 0.51	*9.5*	9.04 ± 0.38
$\beta_3 \times 10^{-11}$	1.90 ± 0.09	1.96 ± 0.10	1.97 ± 0.03	2.00 ± 0.07
$\beta_2 \times 10^{-8}$	3.77 ± 0.22	*3.88*	3.97 ± 0.21	*3.97*
$\beta_1 \times 10^{-4}$	*6.2*	*6.2*	*6.2*	*1 × 10⁻⁴*
$K_4 \times 10^2$	2.07 ± 0.13	2.06 ± 0.15	2.07 ± 0.03	2.21 ± 0.12
$K_3 \times 10^3$	1.99 ± 0.15	1.98 ± 0.10	2.02 ± 0.11	1.99 ± 0.07
$K_2 \times 10^4$	1.64 ± 0.10	*1.60*	1.56 ± 0.08	*3 × 10⁻⁵*
ε_3^{315}	110.6 ± 0.5	110.7 ± 0.5	110.5 ± 0.5	107.8 ± 0.2
ε_2^{315}	82 ± 4	82 ± 4	82 ± 4	91 ± 1
ε_3^{230}	1881 ± 7	1875 ± 7	1890 ± 7	2022 ± 5
ε_2^{230}	700 ± 9	700 ± 9	699 ± 9	525 ± 3
ε_1^{230}	340 ± 20	340 ± 20	330 ± 20	—
$U_{rel} \times 10^2$	3.0	3.0	3.0	3.2
$sigy \times 10^2$	1.10	1.10	1.10	1.12

No value of β_1 can be obtained, since $\bar{n}$ decreases only to about 1.7. In the calculations, β_1 was assigned a constant value of 6.2×10^4 M^{-1}, chosen to give an approximately constant quotient between the stepwise stability constants. The values of the stability constants $\beta_2 - \beta_4$ calculated in columns $1-3$ of Table 2 depend upon this value chosen for β_1, and therefore, have no physical meaning. The stepwise dissociation constants of eqn. (1), $K_n = \beta_{n-1}/\beta_n$, are independent of β_1 for $n > 1$, if β_1 is chosen within reasonable limits.

Table 3. Dissociation constants in M. In the least squares calculations the errors are given as 1σ, in other cases they have been estimated graphically.

Constant Eqn. (1)	60.0°C			25.0°C (Ref. 2)	
	Corresp. solutions	Least squares	Cation exchange	Corresp. solutions	Least squares
$K_4 \times 10^2$	(3.1 ± 0.2)	2.06 ± 0.15	—	1.3 ± 0.1	1.26 ± 0.09
$K_3 \times 10^3$	1.6 ± 0.2	2.00 ± 0.15	—	1.1 ± 0.1	1.40 ± 0.10
$K_2 \times 10^4$	—	1.6 ± 0.1	1.6 ± 0.2	—	1.0 ± 0.1

The dissociation constants obtained are given in Table 3, and the molar absorptivities calculated in columns 1 – 3 of Table 2. In Fig. 1, the functions $\varepsilon_{Pt}(C_{Cl})_{C_{Pt}=\mathrm{const}}$ calculated by the computer using these constants, may be compared to the experimental points. The standard deviation for the differences between calculated and experimental ε_{Pt}'s was 1.1 %. This is about equal to the experimental error in ε_{Pt}.

The formation curve and the distribution of platinum on the different complexes, calculated from the constants obtained, are given in Fig. 2. It appears that the values of $\bar{n}(\log[\mathrm{Cl}^-])$ calculated by the graphical method, especially at 315 nm, deviate somewhat from the formation curve. Accordingly, the value of K_4 obtained by the method of corresponding solutions, is about 30 % greater than that calculated numerically (Table 3). These deviations may be explained by the above-mentioned limitations of the graphical method in this case.

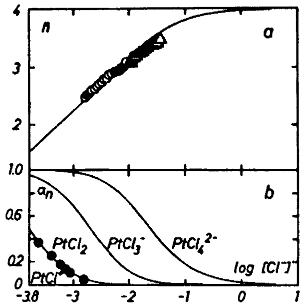

Fig. 2. a. The formation curve at 60.0°C ([Cl⁻] in M), calculated from the constants K_4, K_3, and K_2 obtained by the least squares method (Table 3). The values of $\bar{n}(\log[\mathrm{Cl}^-])$ obtained by the method of corresponding solutions from measurements at 315 nm (△) and 230 nm (○) are also given.

b. The distribution of platinum between different species at 60.0°C. The values of $\alpha_{1\,\mathrm{exp}}$, obtained from the cation exchange measurements, have been marked with ●.

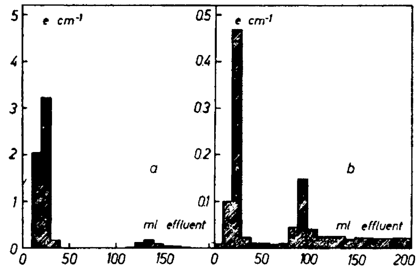

Fig. 3. Two separations using cation exchange columns. The first peak represents $PtCl_4^{2-}+PtCl_3^-+PtCl_2$ and the second, obtained by elution with 3 M $HClO_4$, represents $PtCl^+$. Experimental conditions in Table 4 (experiments marked *a* and *b*).

The equilibrium measurements at 25°C, reported in Ref. 2, were also recalculated using the least squares method. The constants obtained are given in Table 3. The value of K_4 agrees satisfactorily with the graphically calculated one, whereas K_3 differs from it by about 30 % (the two values agree, however, within the limit of 3 σ). An approximate value of K_2 was also obtained from these measurements, indicating the presence of small amounts of $PtCl^+$ in the most dilute solutions even at 25°C. However, none of the solutions used contain more than about 8 % of this complex ($\bar{n}$ decreases to about 2.3), so the constant may possibly have a larger error than indicated in the table.

CATION EXCHANGE MEASUREMENTS

Experimental

Chemicals and apparatus were the same as in Ref. 6. The cation exchange resin, Dowex 50 W× 8, 50–100 mesh, in H^+-form, was washed thoroughly with 5 M HCl, 3 M $HClO_4$ *p.a.*, and water.

Measurements. The solutions of K_2PtCl_4, listed in Table 4, were aged for 3–7 days at (60.0±0.1)°C. They contained no extra chloride. The ionic medium was 0.500 M $HClO_4$. 10–50 ml portions of the equilibrated solutions were rapidly chilled to about 0°C by pouring them into Erlenmeyer flasks, cooled by an ice-sodium chloride mixture. Samples were immediately supplied to the ion exchange column.

The columns had an inner diameter of 12 mm and a length of 27 or 15 mm (Table 4). They were surrounded by cooling jackets containing circulating water at about 6°C, and by aluminium foil to exclude light. The flow rate was about 3 ml min^{-1}.

The effluent was collected in 10 ml volumetric flasks. The column was first percolated with cold water, washing out the anionic and neutral species. The $PtCl^+$ retained by the resin was then eluted by 3 M $HClO_4$. No reduction of Pt(II) occurred in the column. Table 4 shows that within the analytical errors all platinum was refound in the effluent.

Table 4. Cation exchange experiments, giving the mole fraction of $PtCl^+$, $\alpha_{1\,\mathrm{exp}}$. C_{Pt} is in M. Experiments *a* and *b* are shown in Fig. 3*a* and *b*. $\alpha_{1\,\mathrm{calc}}$ was obtained using the values of K_4, K_3, and K_2 calculated from the spectrophotometric measurements by the least squares method.

$C_{\mathrm{Pt}} \times 10^3$	Length of column cm	μ-moles of Pt supplied	μ-moles of Pt in effluent			α_1 exp	α_1 exp Mean	α_1 calc
			1st peak	2nd peak	Sum			
0.988	27	9.88	9.30	0.43	9.73	0.05	0.05	
0.984^a	27	14.76	13.91	0.70	14.61	0.05	±	0.051
0.984	27	19.68	18.54	0.89	19.43	0.05	0.01	
0.500	27	5.00	4.43	0.59	5.02	0.12	0.11	
0.500	15	5.00	4.42	0.57	4.99	0.11	±	0.107
0.500	27	7.50	6.77	0.84	7.61	0.11	0.01	
0.500	15	7.50	6.81	0.80	7.61	0.11		
0.400	15	2.00	1.66	0.28	1.94	0.14	0.14	
0.400	15	4.00	3.47	0.57	4.04	0.14	±	0.133
0.400	15	4.00	3.43	0.53	3.96	0.13	0.02	
0.400	15	6.00	5.11	0.75	5.86	0.13		
0.300	15	1.50	1.13	0.29	1.42	0.20	0.18	
0.300	15	3.00	2.36	0.56	2.92	0.19	±	0.172
0.300	15	4.50	3.63	0.70	4.33	0.16	0.02	
0.200	15	1.00	0.68	0.27	0.95	0.29	0.25	
0.200	15	2.00	1.43	0.52	1.95	0.27	±	0.238
0.200^b	15	2.00	1.45	0.45	1.90	0.24	0.04	
0.200	15	3.00	2.27	0.67	2.94	0.23		
0.100	15	1.00	0.55	0.40	0.95	0.42	0.37	
0.100	15	1.50	0.89	0.57	1.46	0.39	±	0.381
0.100	15	2.00	1.30	0.67	1.97	0.34	0.04	

Analyses. The effluent was analysed for Pt by mixing equal volumes of effluent and 0.500 M HCl. These solutions were kept at 60°C for 12–15 h, and then rethermostated to 25°C for 3–4 h. By this procedure, the platinum of the solutions was converted into an equilibrium mixture consisting of 95 % $PtCl_4^{2-}$ and 5.0 % $PtCl_3^-$ (Ref. 2, Fig. 5) having a molar absorptivity of 7720 cm^{-1} M^{-1} at 230 nm. The absorbance of these solutions at 230 nm gave the concentration of platinum. The error of these analyses was less than 3 %.

Results

In Table 4, the results are given. Fig. 3 shows two experiments. The absorptivities of the solutions, used for the analysis of platinum, have been plotted directly *vs.* the total volume of effluent. The area A_1 under the first peak will be proportional to the amount of $PtCl_4^{2-}+PtCl_3^-+PtCl_2$ present in the initial solution, and that under the subsequent peak, A_2, to the amount of $PtCl^+$. The mole fraction of platinum, present as $PtCl^+$, $\alpha_{1\ \mathrm{exp}}$, was obtained simply as

$$\alpha_{1\ \mathrm{exp}} = A_2 \cdot (A_1 + A_2)^{-1} \tag{3}$$

The areas under the peaks were corrected for a small background absorptivity which was observed in all experiments (Fig. 3). It was probably due to the solubility of the resin in 3 M $HClO_4$ and to a smaller extent in water. This correction became more important for solutions containing small amounts of platinum.

The values of $\alpha_{1\ \mathrm{exp}}$ obtained from eqn. (3) agree excellently with those calculated from the spectrophotometric measurements, given as $\alpha_{1\ \mathrm{calc}}$ in Table 4. In Fig. 2 b, $\alpha_{1\ \mathrm{exp}}$ may be compared to the calculated distribution.

A value of $K_2 = (1.6 \pm 0.2) \times 10^{-4}$ (M) can be calculated by trial and error from $\alpha_{1\ \mathrm{exp}}$ and the spectrophotometrically determined dissociation constants K_4 and K_3 given in Table 3.

DISCUSSION

The cation exchange measurements indicate formation of appreciable amounts of $PtCl^+$ in dilute aqueous solutions of K_2PtCl_4, aged at 60°C. The result of the spectrophotometric measurements are consistent with this model. The mean ligand number, $\bar{n}$, decreases to about 1.7 at 60°C. Even at 25°C, a small percentage of the platinum may be present as $PtCl^+$ at equilibrium in the most dilute solutions used in Ref. 2.

The hydrogen ion concentration of the solutions, 0.500 M, is probably high enough to suppress the hydrolysis of $PtCl^+$ (*cf.* Ref. 1). The fact that this species is retained by a cation exchanger also indicates that it cannot be hydrolysed to a great extent.

It was not possible to detect the tetraaquaplatinum(II)-ion in the concentration range within reach. This is obviously due to the high stability of $PtCl^+$, since the rates of the acid hydrolyses are relatively fast [4] at 60°C. Thus, equilibrating dilute solutions of K_2PtCl_4 at elevated temperatures does not seem to be a possible way of producing measurable amounts of Pt^{2+}. Even if the aging temperature were increased to 100°C (the solutions used endure boiling for some hours without decomposition), it is obvious (*vide infra*) that a 10^{-5} M solution of K_2PtCl_4 would contain at most 50 % Pt^{2+}. This small concentration is not easily accessible by analysis. Some other methods of producing the tetraaquaplatinum(II)-ion in measurable concentration have been tried without success:

(i). The analogous tetraaquapalladium(II)-ion has been prepared[8] from $PdCl_4^{2-}$ by competition for the free chloride ions with Hg(II). Although the platinum complexes too are weaker than those of mercury (*cf.* Table 5), this method cannot be used to produce Pt^{2+}, since platinum is oxidized by Hg(II). Nor is it feasible to use Pd(II) instead of Hg(II), since the palladium complexes are too weak[9] and not transparent in the UV.[10] (ii). It seems likely that attempts to produce Pt^{2+} starting from solutions containing hydroxide complexes of Pt(II) would also be fruitless, since species containing more than two hydroxide ligands per platinum will form polynuclear complexes or even precipitation products.[3,11] (iii). Decreasing the mean ligand number of aged solutions of K_2PtCl_4 by percolating them through anion exhange columns, retaining the free chloride ions, has proved impossible because of the low affinity of chloride to the resins available.

The stability constants of the system could not be calculated from these measurements since K_1 was not obtained. It is reasonable, however, to expect a value of this constant at 60°C of about 1.5×10^{-5} and at 25°C of about 1×10^{-5} M, since the ratios of adjacent stepwise stability constants (or dissociation constants) are usually approximately constant. This is valid, for instance, for the analogous palladium(II) chloro complexes (Ref. 9 and references cited therein). This assumption leads to the stability constants given in Table 5.

Table 5. Estimated stability constants β_n M^{-n}, $n=1, 2, 3, 4$, for the complex formation between Pt^{2+} and Cl^-.

	25°C	60°C
$\beta_1\times10^{-4}$	10	6
$\beta_2\times10^{-8}$	10	4
$\beta_3\times10^{-11}$	7	2
$\beta_4\times10^{-13}$	6	1

The value of β_4 estimated in this way, 6×10^{13} M^{-4} at 25°C, is much smaller than those suggested in the literature. Latimer[12] has calculated a value of about 10^{16} from free energy considerations, but the experimental data used are so uncertain that an error of several powers of ten in his value is possible (*cf.* Ref. 13). Grinberg and Gelfman[14] have calculated a value of $\beta_4=10^{16.6}$ at 18°C from potentiometric measurements, using an "active" platinum electrode in solutions containing $PtCl_4^{2-}$, but Ginstrup and Leden[15] have doubted their results.

The temperature dependence of K_4 and K_3 in the interval 25 – 60°C gives $\Delta H_4 = 3 \pm 1$ and $\Delta H_3 = 2 \pm 1$ (kcal mol^{-1}) as approximate values of the enthalpy changes for the substitution of chloride by water in $PtCl_4^{2-}$ and $PtCl_3^-$. ΔH_2 is positive also, and of the same magnitude as ΔH_3 and ΔH_4. These values are similar to those of the analogous Pd(II) chloro complexes, having stepwise dissociation enthalpies, $\Delta H_4 - \Delta H_1$, of about 3 kcal mol^{-1} (Ryhl [16]).

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