

Preparation and Properties of the Tetra-aquaplatinum(II) Ion in Perchloric Acid Solution

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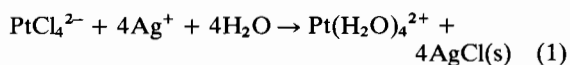
Dilute solutions of the square-planar tetra-aqua complex $Pt(H_2O)_4^{2+}$ have been prepared in a 1.00 M perchloric acid medium by addition of excess silver(I) perchlorate to potassium tetrachloroplatinate(II), equilibration at 70°C, filtration of the silver chloride precipitate, and subsequent separation of the excess silver from the solution by electrolysis. The complex has also been prepared by addition of mercury(II) perchlorate to tetrachloroplatinate(II) solutions. The UV and visible absorption spectrum of the complex has been recorded and its hydrolysis qualitatively studied. The experiments indicate that $Pt(H_2O)_4^{2+}$ is a weak acid with $pK_a > 2.5$. A white, amphoteric hydroxide of platinum(II) is precipitated in the pH region 4 to 10.

Introduction

The only square-planar tetra-aqua complex described in the literature so far is $Pd(H_2O)_4^{2+}$ (cf. Refs. 1, 2 and papers cited therein). The kinetics for its halide anation reactions have been studied.^{3,4} The present communication reports the preparation of the previously unknown tetra-aqua ion of platinum(II), $Pt(H_2O)_4^{2+}$, and will be followed by a paper on the kinetics and mechanism for some anation reactions of this complex.⁵

Mixed chloro-aqua complexes $PtCl_n(H_2O)_{4-n}^{2-n}$, $n = 1, 2, 3, 4$, are formed by a series of stepwise acid hydrolysis reactions in dilute solutions of tetrachloroplatinate(II) in perchloric acid aged at elevated temperatures⁶. Because of the stability of $PtCl(H_2O)_3^+$, however, it is not feasible to obtain more than micromolar solutions of $Pt(H_2O)_4^{2+}$ by the previously used technique for dilution and ion-exchange separation.⁶

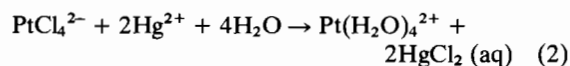
In a perchloric acid solution of tetrachloroplatinate(II) containing excess silver perchlorate, the reaction



takes place slowly. After equilibration and subsequent filtration of the silver chloride precipitate, the excess

silver can be separated quantitatively from the solution by electrolysis. The resulting solution contains only potassium, hydrogen and perchlorate ions in addition to $Pt(H_2O)_4^{2+}$.

Addition of a slight excess of mercury(II) perchlorate to perchloric acid solutions of tetrachloroplatinate(II) can also be used for preparation of $Pt(H_2O)_4^{2+}$:



This process is relatively fast, since mercury(II) ions accelerate the stepwise acid hydrolysis reactions of the platinum(II) chloro complexes.

Experimental

Chemicals and Equipment

Potassium tetrachloroplatinate(II) (Johnson and Matthey) was used without further purification. Its UV spectrum was identical with previously recorded spectra for recrystallized preparations.⁷ *Anal.*: Pt (46.78 ± 0.08)%, Cl (34.02 ± 0.03)%. Calc. for K_2PtCl_4 : Pt 47.00%, Cl 34.16%.

Approximately 0.20 M solutions of silver perchlorate (G. F. Smith, reagent quality) in 1.00 M perchloric acid were standardized electrometrically. Solutions of mercury(II) perchlorate were prepared by dissolution of yellow mercury(II) oxide (Merck *p.a.*) in 1.00 M perchloric acid.

Perchloric acid (Baker's *p.a.*), hydrochloric acid (Merck's *p.a.*) and water, doubly distilled from quartz vessels, were used to prepare solutions. All other chemicals were reagent grade.

Spectra were recorded using a Cary 14 recording spectrophotometer.

Preparation Using Silver(I)

About 3.5 g (8.5 mmol) potassium tetrachloroplatinate(II) was added to 400.0 ml 1.00 M perchloric acid in a 1000 ml flask with glass stopper. The mixture was flushed with carbon dioxide or argon to prevent oxidation, placed in a dark air-thermostat at about

70°C and stirred for 60 to 90 minutes. All potassium tetrachloroplatinate(II) dissolved.

According to the equilibrium constants given in Ref. 6, about 5 mmol of chloride is released from PtCl_4^{2-} in this solution by acid hydrolysis. 400.0 ml of 0.20M silver perchlorate was added slowly over a period of 6 to 7 hours, first using four 25 ml portions (*i.e.* about 5 mmol of silver each), then 50 or 100 ml portions, with continuous stirring. Between the additions of silver perchlorate the mixture was flushed with carbon dioxide/argon, kept in the thermostat at 70°C for about one hour, and stirred. The slow addition of silver at the beginning of the procedure was necessary in order to prevent precipitation of the sparingly soluble Ag_2PtCl_4 . The mixture was then kept under carbon dioxide/argon at 70°C in the dark and stirred for about 6 days. Variation of the aging time between 5 and 20 days showed that the reaction was complete within this time. The excess concentration of silver ions of about 60 mM is sufficient for the acid hydrolysis reactions to give the complex $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ quantitatively according to reaction (1) (*vide infra*). After aging the mixture was cooled to about 0°C. The precipitate was filtered off, washed, dissolved quantitatively in 1M sodium cyanide and analyzed for silver by electrolysis (*cf.* Table I).

The filtrate, containing about 10 mM platinum(II), 60 mM silver, 20 mM potassium and 1M perchloric acid was transferred quantitatively to a 1000 ml three-necked flask and electrolyzed at room temperature. The cathode was a cylindrical platinum net electrode 18 × 40 mm. The anode was a 20 × 20 mm platinum sheet, immersed in 1.00M perchloric acid in an electrode compartment, which was separated from the main solution by a glass filter disk. Bright silver crystals precipitated at the cathode at a voltage of (1.37 ± 0.01) V. The current was about 30 mA. The electrolysis continued for about 75 hours. The current decreased to less than 5 mA. Small quantities of platinum also deposited at the cathode, especially during the final period of the electrolysis. The silver deposit was dissolved in 1M nitric acid. This solution was neutralized and analyzed for silver by electrolysis in 1M sodium cyanide solution (*cf.* Table I).

The resulting platinum(II) perchlorate solution was filtered and kept in a stoppered flask under carbon dioxide/argon at about 4°C in a refrigerator. Solutions handled in this manner were stable for more than one year. No oxidation, disproportionation or precipitation could be observed. The color of an about 8 mM solution was bright yellow, very similar to that of palladium(II) perchlorate solutions of the same concentration.^{1,2} Figure 1 shows the absorption spectrum. Spectra recorded using solutions flushed with carbon dioxide were identical with those obtained for solutions flushed with argon, *i.e.* no carbonate complexes were formed in these acidic solutions.

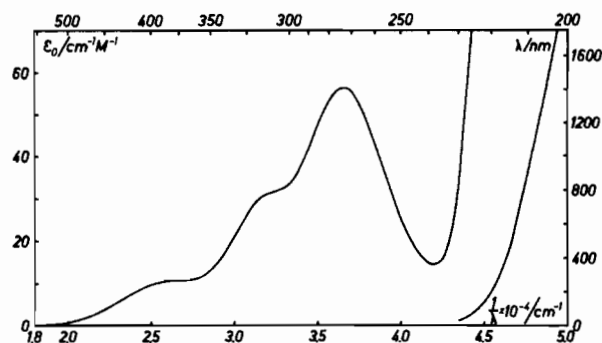


Figure 1. Absorption spectrum for $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in 1.00M perchloric acid recorded using one 4 mM and one 8 mM platinum(II) perchlorate solution, prepared by addition of silver. The reference was 1.00M perchloric acid.

Preparation Using Mercury(II)

A solution of mercury(II) perchlorate (2.5 to 100 mM) in 1.00M perchloric acid was added dropwise over 5 to 10 minutes to a stirred solution of potassium tetrachloroplatinate(II) (1 to 10 mM) in 1.00M perchloric acid at room temperature. The pink platinum solution immediately turned yellow. After mixing the total concentrations were $0.5 \text{ mM} < C_{\text{Pt}} < 4 \text{ mM}$ and $1 \text{ mM} < C_{\text{Hg}} < 6 \text{ mM}$.

For $C_{\text{Hg}}/C_{\text{Pt}}$ 0.5 or 1.0, the spectrum of the resulting solution resembled that of $\text{PtCl}_3\text{H}_2\text{O}^-$ or $\text{PtCl}_2(\text{H}_2\text{O})_2$, respectively.⁷ These spectra were obtained rapidly, within the time of mixing.

For $C_{\text{Hg}}/C_{\text{Pt}} = 1.5$ the spectrum resembled that of $\text{PtCl}(\text{H}_2\text{O})_3^+$,⁸ and for ratios > 2.0 , $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ -spectra were obtained. The latter reactions required 5 to 10 hours to go to completion. The equilibration time decreased for large concentrations of mercury and for illumination of the solutions by UV light or even by diffuse daylight. Figure 2 shows the spectra recorded using blanks containing mercury(II) and chloride in appropriate concentrations.

A brown precipitate was formed slowly in all solutions containing mercury. For mercury concentrations about 1 mM, the spectrum of the solution was constant, and several days elapsed before precipitation was observed, but for 10 to 20 mM solutions, precipitation occurred already after a few hours and the absorbance of the solution increased slowly with time. The $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ spectrum in Figure 2 recorded using 1.25 mM mercury concentration, has molar absorptivities 5 to 10% larger than the spectrum in Figure 1 for a solution prepared by the silver method. This small deviation probably indicates a beginning precipitation in the mercury-containing solution (*vide infra*). Disregarding this discrepancy, however, the spectra for $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ obtained by the two independent methods of preparation have exactly the same shape.

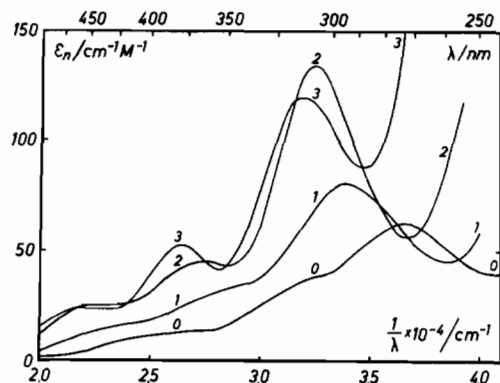


Figure 2. Absorption spectra for solutions with different ratios $C_{\text{Hg}}/C_{\text{Pt}}$:

Number	C_{Hg}/mM	C_{Pt}/mM	$C_{\text{Hg}}/C_{\text{Pt}}$
3	1.00	2.00	0.50
2	1.00	1.00	1.00
2	2.00	2.00	1.00
1	3.0	2.00	1.50
1	6.0	4.0	1.50
0	1.25	0.51	2.4

The spectrum marked 0 is identical to that shown in Figure 1 except that the ϵ values are 5 to 10% larger. The reference was 1.00M perchloric acid, containing mercury(II) and chloride in appropriate concentrations.

Analyses

The spectrum of PtCl_4^{2-} reappeared when the platinum(II) perchlorate solutions prepared by the two methods were mixed with equal volumes of 1.00M hydrochloric acid and heated to 60°C for 12 to 15 hours. All platinum was recovered as PtCl_4^{2-} , and no extra absorbance was observed at the maximum for PtCl_6^{2-} at 262 nm.

Table I shows typical analysis results for solutions prepared by addition of silver(I). It is obvious that within the experimental errors, all added silver was recovered as silver chloride or metal, and all chloride in the tetrachloroplatinate(II) as silver chloride.

Direct determinations of chloride and silver in the solutions prepared by the silver method were also performed. A 7 mM platinum(II) perchlorate solution was electrolyzed for 2 hours at 2.0 V. All platinum deposited at the cathode. The colorless solution was analyzed for chloride by titration with standard silver nitrate. No chloride was detected.

Since the platinum complexes react slowly with chloride,^{5,9} the platinum(II) perchlorate solutions could be analyzed for free silver ions simply by addition of chloride. No precipitate of silver chloride was obtained.

Results and Discussion

The good agreement between the absorption spectra of the final solutions (cf. Figure 1 and curve 0, Figure 2) indicates that the two methods of preparation give the same platinum complex as reaction products. The quantitative reversibility to PtCl_4^{2-} shows that no oxidation or disproportionation of platinum(II) occurs during the preparation.

It is obvious from the chloride analyses of the solutions prepared by the silver method that the dissociation of the chloride ligands from PtCl_4^{2-} according to reaction (1) was practically complete, giving a mean ligand number for chloro complexes of less than 0.01 in the final solutions. This result is reasonable, both if kinetics and equilibria are considered. The rate-determining steps for the consecutive dissociations of the complexes under the experimental conditions used will be the acid hydrolyses of *cis*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ and $\text{PtCl}(\text{H}_2\text{O})_3^+$ with rate constants of about $3 \times 10^{-7} \text{ s}^{-1}$ at 25°C and 0.5M perchloric acid medium according to the reaction model in Ref. 9, Figure 9. The rate constants at 70°C can be estimated to about $3 \times 10^{-5} \text{ s}^{-1}$, which gives a half-life for the formation of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ via these two consecutive processes of about 15 hours (cf. Ref. 10). The reaction should therefore be complete within the equilibration time of six days. If silver ions and solid silver chloride accelerate the acid hydrolyses, as has been observed for reactions of

TABLE I. Analytical Results for Solutions Prepared by Addition of Ag(I). The volume of the final solution was 800 ml.

Cl Added mmol (as K_2PtCl_4)	Ag Added mmol (as AgClO_4)	AgCl mmol	Ag Electrolyzed mmol	Ag Difference mmol	Cl Difference mmol	C_{Pt}/mM (final soln)
33.62	78.77	33.22	45.42	0.13	0.40	7.54
33.67	78.77	33.45	45.45	-0.13	0.22	8.76
33.78	78.68	33.46	45.09	0.13	0.32	4.82
33.72	74.03	33.91	39.95	0.17	-0.19	6.97
33.81	76.39	33.27	42.66	0.46	0.54	9.16
33.65	76.39	33.49	42.57	0.33	0.16	9.28

cobalt(III) complexes,¹¹ the equilibration time might be even shorter.

The solubility product for silver chloride in 1M perchloric acid can be estimated to about $10^{-8} M^2$ at 70°C. The excess concentration of silver ions of about 60 mM used in the synthesis will therefore give a concentration of free chloride of about $2 \times 10^{-7} M$. This concentration should be small enough to suppress the mean ligand number for platinum(II) chloro complexes below 0.01, if the previous estimation of the stability constant for $PtCl(H_2O)_3^+$ of $6 \times 10^4 M^{-1}$ at 60°C is correct.⁶

The *d-d* spectrum for $Pt(H_2O)_4^{2+}$ shown in Figure 1 has three absorption bands. A Gaussian analysis of the spectrum gave the energies and molar absorptivities listed in Table II. As in the case of $Pd(H_2O)_4^{2+}$,^{1,2} the first charge-transfer band for $Pt(H_2O)_4^{2+}$ lies beyond 200 nm.

The absorption spectra for the mixed chloro-aqua complexes of platinum(II) will be discussed subsequently.⁸ The data given in Table II for the *d-d* transitions indicate clearly that there is a regular shift of the maxima for the three bands from $PtCl_4^{2-}$ to $Pt(H_2O)_4^{2+}$ according to the rule of average environment. Band number 2 corresponds to a singlet \rightarrow triplet transition, number 3 to a transition $d_{xy} \rightarrow d_{x^2-y^2}$, and number 4 to transitions from d_{xz} , d_{yz} and d_{z^2} to $d_{x^2-y^2}$.⁸

Hydrolysis

The spectrum of an 8 mM platinum(II) perchlorate solution in 1.00M perchloric acid (*vide* Figure 1) remained constant for more than one year. Solutions with hydrogen ion concentrations of 1.0, 3.0 and 4.5M (prepared using an 8M sodium perchlorate medium) gave practically identical spectra. Partial neutralisation of the platinum(II) perchlorate solutions in 1M perchloric acid with solid sodium hydrogen carbonate to pH 1 to 2.5 also gave absorption spectra identical to that in Figure 1. A formation of mononuclear hydroxo complexes should displace the absorption bands of $Pt(H_2O)_4^{2+}$ towards the UV. No such shift was observed in the pH range studied. Thus,

it can be inferred that the protolysis of the aqua ligands of $Pt(H_2O)_4^{2+}$ is negligible for pH < 2.5.

A slow formation of polynuclear or even colloidal species probably occurred in solutions having pH > 1. It was revealed by a slow, general increase of the absorption spectrum in the whole wavelength interval studied, especially evident at the absorbance minimum for $Pt(H_2O)_4^{2+}$ at 240 nm (similar for $Pd(H_2O)_4^{2+}$, *cf.* Refs. 1, 2). The somewhat larger molar absorptivities for the $Pt(H_2O)_4^{2+}$ solutions prepared by addition of mercury(II) (*cf.* Figure 2) can also be explained by the presence of colloidal species.

If the pH for a platinum(II) perchlorate solution with pH = 0 was suddenly changed to 12 or 14 by addition of 1M sodium hydroxide, slow and irreproducible changes of the spectra were observed. When the pH was rapidly decreased to zero again by addition of perchloric acid the spectrum indicated that polynuclear or colloidal hydrolysis products had been formed.

Figure 3 shows a potentiometric titration with sodium hydroxide of a platinum(II) perchlorate solution flushed with argon. A white, amphoteric hydroxide precipitated at about pH 4 and redissolved at about pH 10. The titration was reversible in the pH region 1 to 3.5 without noticeable hysteresis, if titration and

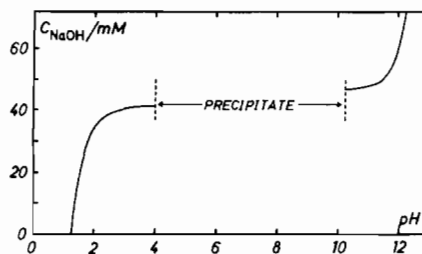


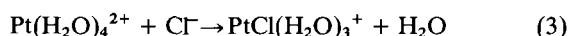
Figure 3. Titration of 10.00 ml of a 9.35 mM platinum(II) perchlorate solution in 1.00M perchloric acid, flushed with argon. The strong acid was first partly neutralized by addition of 9.00 ml 0.991M sodium hydroxide. The titration was then performed using 0.0991M sodium hydroxide. About 3 mol hydroxide per platinum were consumed in the pH region 4 to 10.

TABLE II. Energies in kK and (within parenthesis) Molar Absorptivities in $cm^{-1} M^{-1}$ for the *d-d* Transitions of Mixed Chloro-Aqua Platinum(II) Complexes.

Complex	<i>d-d</i> Transition				Ref.
	1	2	3	4	
$PtCl_4^{2-}$	17.8(3.2)	21.0(17)	25.6(56)	30.2(59)	7
$PtCl_3(H_2O)^-$	—	21.4(19)	26.1(48)	31.4(107)	7
<i>cis</i> - $PtCl_2(H_2O)_2$	—	22.5(20)	26.9(25)	32.5(170)	8
<i>trans</i> - $PtCl_2(H_2O)_2$	—	22.5(10)	28.1(35)	33.1(40)	8
$PtCl(H_2O)_3^+$	—	—	28.5(25)	34.3(87)	8
$Pt(H_2O)_4^{2+}$	—	25.7(10)	31.3(15)	36.6(56.5)	This paper

back-titration were performed rapidly to minimize polynuclear hydrolysis. There was no evidence for protolysis of acidic aqua complexes in the pH region 1 to 3.

Both the titration and the constancy of the Pt $(\text{H}_2\text{O})_4^{2+}$ spectrum for $\text{pH} < 2.5$ indicate that Pt $(\text{H}_2\text{O})_4^{2+}$ is a relatively weak acid with a pK_a greater than at least 2.5. This is also supported by the fact that the observed rate constant for the anation



is independent of pH in the interval 0 to 2 (*cf.* Ref. 5). All these observations suggest that both the mono- and polynuclear hydrolyses of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ are very similar to those of the corresponding palladium complex.^{1,2,12}

The freshly precipitated white hydroxide could be filtered and washed with alcohol and acetone. When dried at 100°C, it lost 7 to 10% in weight and gave rapidly a black residue, probably a platinum(II) oxide, which dissolved in 5M hydrochloric acid but not in concentrated perchloric acid. Even at room temperature the white precipitate slowly turned black.

The hydroxide dissolved easily in 1M perchloric acid and 1M sulfuric acid. A minor change with time of the spectra for solutions prepared in this way was observed during one day, concordant with a slow decomposition in the 1M acid of polynuclear or colloidal species present in small amounts, but finally the $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ spectrum was obtained. The sulfuric acid spectrum gave no evidence for inner-sphere sulfato complexes, even when excess sodium sulfate was added, in similarity with palladium(II) sulfate solutions.² The hydroxide dissolved in 1M hydrochloric or hydrobromic acid and in 1M sodium cyanide, giving slowly the tetrahalo and tetracyano complexes.⁵ It also dissolved

in 1M sodium hydroxide, giving a solution with a slowly changing spectrum, due to polynuclear hydrolysis.

Kinetic studies using $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ as substrate complex and different entering ligands have been completed and are reported subsequently.⁵

Acknowledgments

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