

An EXAFS study of the co-ordination chemistry of hydrogen hexachloroplatinate(IV)

1. Speciation in aqueous solution

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Abstract

Hydrogen hexachloroplatinate(IV), also called chloroplatinic acid (CPA), is a strong acid that undergoes rapid and extensive hydrolysis. Extended X-ray absorption fine structure (EXAFS) characterization was performed at the Advanced photon source (APS) at Argonne National Laboratory to determine the Pt–Cl and Pt–O co-ordination chemistry of 200–2000 ppm CPA at pHs of 1.5–12 with different chloride concentrations, light conditions, and time frames. The EXAFS analysis was combined with potentiometric data to postulate the following speciation behavior of the dilute CPA. The initial hydrolysis reaction, aquo ligand exchange of chloride ions, is rapid and reversible, while the latter two reactions, hydroxide ion ligand exchange of chloride and aquo ligands, are relatively slow in acidic solutions but accelerated in the presence of light. Many of the stable Pt complexes in solution are zero valent. High chloride co-ordination is favored at low pH and high chloride concentration. As a result, the $[\text{PtCl}_6]^{2-}$ species is present only in acidic solutions with a moderate excess of chloride ion or in the neutral solutions in a large excess of chloride ion. Hydroxide ligand formation is favored at low pH and suppressed by chloride ion concentration. As a result, full hydrolysis of CPA by hydroxide ions with precipitation of $\text{H}_2\text{Pt}(\text{OH})_6$ (or $\text{Na}_2\text{Pt}(\text{OH})_6$) is favored only at very low CPA concentrations (ca. 30 ppm). © 2002 Published by Elsevier Science B.V.

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1. Introduction

Hydrogen hexachloroplatinate(IV), H_2PtCl_6 , (also called chloroplatinic acid, CPA) is one of the most frequently used compounds for the preparation of supported platinum catalysts. The principal commercial application for Pt catalysts in the refining industry is naphtha reforming, where small metallic Pt

particles are supported on high surface area, chlorided γ -alumina. In order to obtain highly dispersed Pt particles, it is first necessary to uniformly deposit CPA on the alumina surface. Subsequent pre-treatment with air (calcination) and hydrogen (reduction) leads to Pt particles smaller than 10 Å that are highly active and selective.

For a fundamental understanding of catalyst impregnation via the dissolution of CPA in H_2O , it is necessary to determine which species are present and how they interact with the support. CPA is hygroscopic and readily dissolves in water. While the degree of

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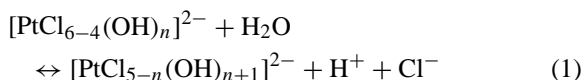
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dissociation of the diprotic acid is unclear, it is generally agreed that CPA solutions are acidic. In addition, it is generally agreed that the Pt–Cl bonds undergo a series of hydrolysis reactions in aqueous solution [1–5]. Either hydroxyl groups or water molecules may replace the chloride ligands. Ligand exchange of Cl^- ion by H_2O results in an increase in the charge on the Pt complex; the exchange by hydroxide ion does not affect the charge, but it leads to a decrease in the pH. In both cases, hydrolysis also results in an increase in the solution chloride concentration. It is also generally agreed that the octahedral co-ordination of the Pt(IV) complex is stable in virtually all solution conditions.

The effect of pH on the speciation of the metal complex is especially important, since; oxides used as catalyst supports can dramatically alter the impregnating solution pH due to their strong buffering effect [6,7]. For example, the pH of Pt-containing solutions used for incipient wetness impregnation (an amount of liquid equal to the pore volume) of alumina will change from about 2 to 8 due to the consumption of protons by the surface hydroxyl groups [7]. The addition of support oxides with a basic point of zero charge (PZC) to an impregnating solution can have the same effect as an increase in the solution pH. Similarly, the Pt species present in acidic solutions will be similar to those present when Pt solutions are added to supports with an acidic PZC. Studies of liquid phase speciation as a function of pH should then mimic, at least in part, the phenomena occurring during catalyst impregnation.

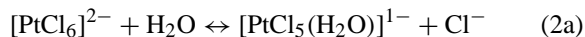
There are various pathways of CPA speciation and sets of formation constants available in the literature. The oldest work is that of Miolati and Pardini [8] and earlier references within; this pathway is cited in Gmelin's handbook [2], and most recently, in the review of Boitiaux et al. [5]. In the Miolati series, the sequence of ligand exchange reactions can proceed stepwise from $[\text{PtCl}_6]^{2-}$ to the insoluble $[\text{Pt}(\text{OH})_6]^{2-}$. In addition, chlorine ligands are exchanged exclusively by hydroxide ions, which also leads to a decrease in the pH of the aqueous solution. The degree of hydrolysis was determined via the electric conductivity of the solution, essentially giving a measure of the chloride concentration. Hydrolysis is proposed to occur as follows:



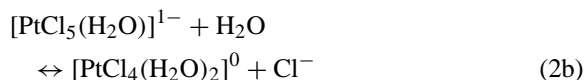
where $n = 0, 1, 3, 4$ or 5 depending on pH and concentration [2]. This model is only qualitative, since, no equilibrium constants are given. In a dilute solution of 0.0001 M (roughly 20 ppm Pt), the hydrolysis eventually led to the formation of a reddish brown precipitate, $\text{H}_2\text{Pt}(\text{OH})_6$. Higher concentration solutions of 0.01 and 0.1 M (2000 and 20,000 ppm) were reported to be more stable.

The final CPA hydrolysis steps are reported to be kinetically slower, but they can be significantly accelerated by UV light ($\lambda = 253.6$ nm). A 3 days exposure of a freshly prepared 0.001 M solution to sunlight almost tripled the electrical conductivity, while the conductivity of an identical solution kept in the dark over 5 days increased only 4% [2]. Another group also reported the formation of $[\text{PtCl}_5(\text{OH})]^{2-}$ through flash photo excitation of Na_2PtCl_6 solutions [9].

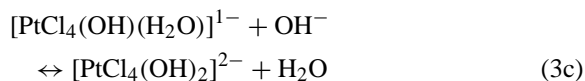
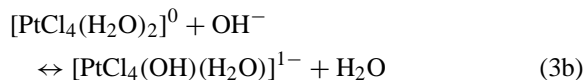
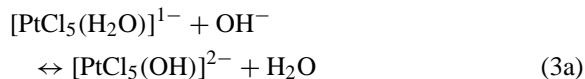
A more recent and commonly cited pathway and set of equilibrium constants is that of Sillen and Martell [1], obtained by UV–VIS spectroscopy. This model of CPA speciation was employed by Anderson [4] and Boitiaux et al. [5] in their reviews. The mechanism consists of two hydrolysis steps in which chloride is replaced by water as follows:



and



These aquo complexes are thought to behave as weak acids and rapidly dissociate in basic solutions:



The resulting Pt species predicted from this model at different pH values are shown in Fig. 1. Dissociation of the acid is presumed complete. The degree of ligand exchange increases to a maximum of two exchanged

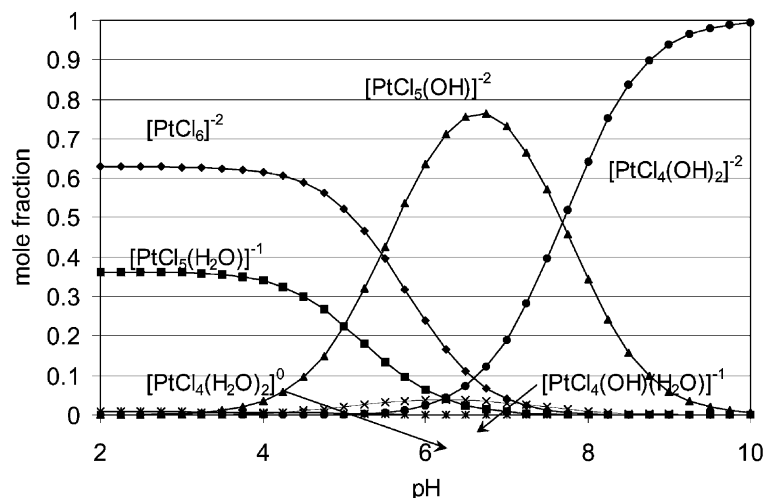


Fig. 1. Pt speciation from the pathway and formation and dissociation constants of Sillen and Martell.

chlorides as solutions become basic. In acidic solution, Cl^- ions are exchanged by water. As the solution becomes more basic, the aquo complexes are assumed to deprotonate as weak acids to yield the respective hydroxo complexes. The equilibrium constants were determined at low pH and high Pt concentrations; it is likely that they accurately predict the Pt species only in acidic to neutral aqueous solutions. The authors acknowledge that more extensive hydrolysis is probable at higher pH, leading to $[\text{Pt}(\text{OH})_6]^{2-}$ in strongly basic solution, but no experimental evidence was given.

A yet more recent report of Knözinger and co-workers [3] employs the same pathway as Sillen and Martell [1], but with the pentachloro formation and acid dissociation constants of Davidson and Jameson [10], which were determined by potentiometry and spectrophotometry, and the tetrachloro-diaquo stepwise acid dissociation constants of Cox and Peters [11], determined potentiometrically for the *trans* complex. This model predicts vastly different species than those from Sillen and Martell's constants. According to this model (Fig. 2 of [3]), at low pH a large fraction of the CPA remains protonated (i.e. CPA is a weak acid). Almost no $[\text{PtCl}_6]^{2-}$ exists in solution at any pH. Below $\text{pH} \approx 2$, there is no hydrolysis, and in weakly acidic solutions, one chloride ion is exchanged by water. As with Sillen and Martell's model above, in basic solutions, up to two Cl ligands can undergo hydrolysis, and water ligands are fully deprotonated.

A further complication is that the tetrachloro complexes can exist in various isomers with the water or hydroxyl ligands in the *cis* or *trans* configuration. An early ^{195}Pt NMR study assigned signals to *cis* and *trans* chlorohydroxo complexes at high pHs, and to *cis* and *trans* chloroaquo complexes at low pHs [12]. This study also confirmed high levels of chloride exchange, through $[\text{Pt}(\text{OH})_6]^{2-}$ at high pH, and through $[\text{PtCl}_2(\text{H}_2\text{O})_4]^{2+}$ at low pH (the penta and hexaquo complexes being insoluble at low pH [12]).

The most recent study of CPA speciation in the liquid phase was that of Lambert and co-workers [13] using ^{195}Pt NMR. They adopt the same basic pathway as Sillen and Martell (Fig. 1). Using a fit of the shift of NMR signals of the tetrachloride species, they arrived at a set of formation and acid dissociation constants for species including the *cis* and *trans* tetrachloride isomers. Some of their derived constants are considerably different from earlier values.

In our work, the influence of platinum concentration, pH, chloride concentration, aging, and exposure to laboratory light on the aqueous solutions of relatively dilute CPA was investigated by EXAFS spectroscopy. While NMR has the advantage of being able to discriminate between (OH) and (H₂O) ligands, its sensitivity relative to EXAFS at the advanced photon source (APS) is much lower and is, thus, limited to relatively high Pt concentrations (over 2400 ppm). (Lambert and co-workers utilized EXAFS to characterize

adsorbed CPA species in later work [14,15]). We characterized CPA solutions from 200 to 2000 ppm, which are similar to the concentrations employed in many laboratory [3,16,17] and references therein and industrial catalyst preparations [4,5]. The results for these dilute solutions confirm that H_2PtCl_6 undergoes hydrolysis to a much greater extent than do more concentrated solutions. The EXAFS and pH measurements suggest that the initial Cl ligand exchange occurs with water and that at longer times hydroxide ions can exchange for either water or chloride ligands. A comprehensive speciation pathway is presented which accounts for both concentrated and dilute CPA solutions. These results form the basis for a companion study of Pt complexes adsorbed onto alumina [18].

2. Experimental

2.1. Preparation of CPA solutions

Aqueous solutions of hydrogen hexachloroplatinate(IV) hydrate (Aldrich) were dissolved in deionized water at room temperature. The Pt concentration was varied from 30 to 2000 ppm Pt. HNO_3 , HCl , NaOH , and NaCl were added to adjust the pH and Cl level. Most samples were prepared within 1 h before EXAFS data acquisition under normal laboratory lighting. Freshly pH-adjusted solutions prepared from fresh CPA solutions, are referred to as “fresh/fresh” in the discussion to follow. Two series of aged, 200 ppm CPA solutions were also prepared. In one, portions of a freshly prepared solution were pH-adjusted to various values, these solutions were aged for 2 weeks. This series is referred to as “fresh/aged”. In the second, the solution was aged at the “natural pH” of CPA. The natural pH is defined to be the pH resulting from the addition of solid CPA to distilled, deionized water (with an initial pH of about 5.8). For a 200 ppm Pt solution, this value is about 2.7 immediately after the addition but, as will be shown later, it drifts down several tenths of a pH unit over the course of about 24 h. The aged solution was pH-adjusted to various values just before analysis. This solution is “aged/fresh”. Finally, several aged/fresh 200 ppm CPA solutions were prepared and analyzed in the absence of visible light.

2.2. EXAFS analysis

EXAFS measurements were performed at the Materials Research Collaborative Access Team (MRCAT) undulator beam-line equipped with a double-crystal $\text{Si}(111)$ monochromator with a resolution better than 4 eV at 11.5 keV (Pt L_3 edge). A Rh-coated mirror was used to minimize the presence of harmonics. Spectra of the Pt solutions were taken in fluorescence mode using the Stern and Heald configuration [19] with a 0.1 mm high-purity Zn foil filter. The resulting signal-to-background ratio was approximately 0.8 from a 1 cm 200 ppm Pt solution.

Standard procedures were used to analyze the EXAFS data using WinXAS 97 software [20]. Phase-shift and backscattering amplitudes were obtained from the reference compounds: solid samples of $\text{Na}_2\text{Pt}(\text{OH})_6$ for Pt–O and H_2PtCl_6 for Pt–Cl. Fig. 2a shows the k^2 -weighted EXAFS data of the 200 ppm CPA solution at a pH of 1.5 in HCl . The magnitude and imaginary part of Fourier transform was fit in r -space ($\Delta r = 1.29 - 2.32 \text{ \AA}$), a typical fit is shown in Fig. 2b. Several assumptions were made to simplify the EXAFS fits. First, since, Pt (IV) complexes are typically octahedral, it was assumed that the sum of the Pt–Cl and Pt–O co-ordination numbers was six for all complexes. This assumption is reasonable, since, the total co-ordination numbers of all samples in this study were between 5.8 and 6.5 if this parameter was allowed to vary. In the fits, the Pt–Cl and Pt–O bonds were also fixed at 2.32 and 2.05 \AA , respectively. These distances are identical to those in the H_2PtCl_6 and $\text{Na}_2\text{Pt}(\text{OH})_6$ reference compounds. In a typical fit, the bond distances were within 0.02 \AA of these values if allowed to float. However, small changes in either bond distance resulted in small changes in the co-ordination numbers. Therefore, in order to more consistently determine changes in the co-ordination sphere, the bond distances were assumed to be constant in all complexes. Changes in the Debye–Waller (DW) factor also affect the co-ordination number in the model fit. Since, the reference compounds and samples are very similar (solids versus solutions of the same compounds), the DW factor is generally small. For a given sample, the DW factor differences of Pt–Cl and Pt–O were assumed to be equal. This constraint typically led to a total co-ordination number near 6.0, which seems reasonable. The final fit parameters fit equally well

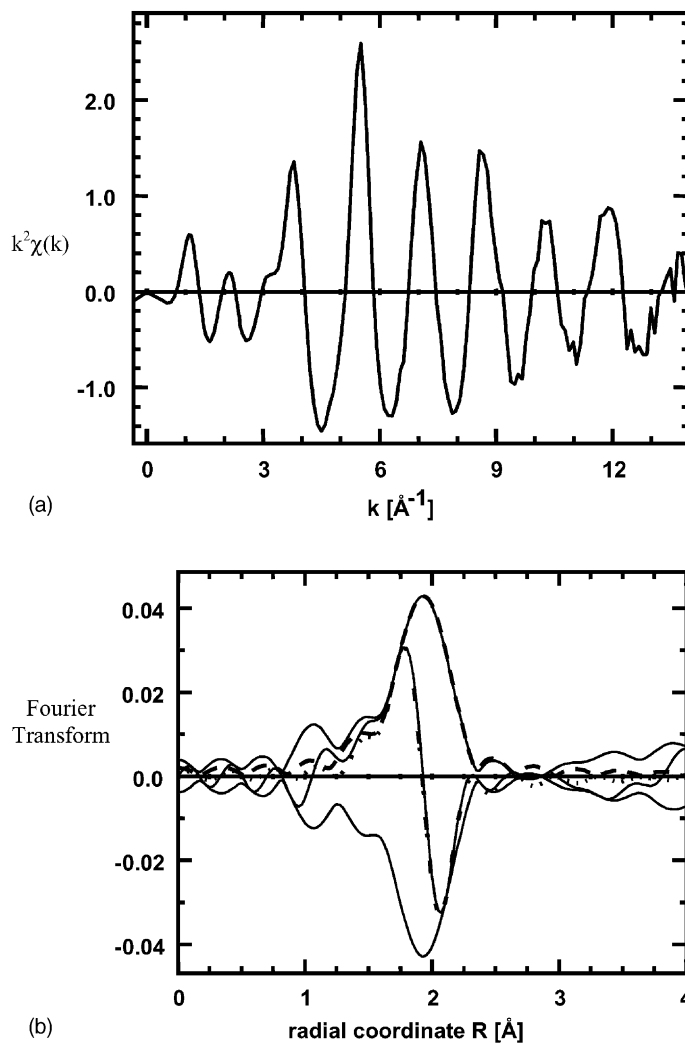


Fig. 2. (a) Raw EXAFS data, 200 ppm CPA solution at pH = 1.5 HCl; (b) typical fit of EXAFS spectrum, for 200 ppm CPA at pH = 1.5 HCl (data: solid- and fit-dashed; k^2 , $\Delta k = 3.0$ – 10.7 , $\Delta r = 1.0$ – 2.7).

with k^1 – k^3 weighting. The co-ordination number results were accurate to about 0.3.

3. Results

Fourier transforms of the EXAFS spectra of 200 ppm Pt solutions, at a pH of 1.5 (in HCl), at its natural pH of 2.7, and at a pH of 12 (in NaOH), are shown in Fig. 3. The spectrum of CPA in HCl at a pH of 1.5 is characteristic of Pt with a high co-ordination

of Cl bonds and is nearly identical to the solid CPA reference. For CPA at pH 12, the reliable data range was limited to when $k \cong 9 \text{\AA}^{-1}$, and the magnitude of the Fourier transform was shifted to a shorter distance, characteristic of a large number of Pt–O bonds. The spectrum for fresh CPA at its natural pH (about 2.7) indicates a co-ordination geometry intermediate between the two. The fits of the Pt co-ordination geometry are consistent with octahedral co-ordination, thus, at a pH of 1.5 in HCl, CPA is present at PtCl_6^{2-} , while at a pH of 12, the average Pt co-ordination is

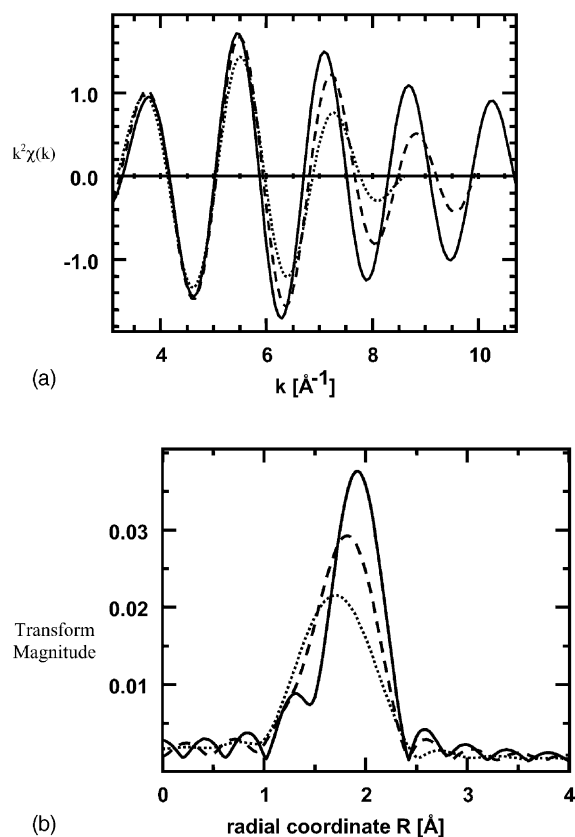


Fig. 3. (a) EXAFS of Pt co-ordination sphere: solid-CPA at pH = 1.5 HCl (k^2 , $\Delta k = 3.0$ – 10.7 ; $\Delta r = 1.0$ – 2.7); dashed-CPA at pH = 2.6 (k^2 , $\Delta k = 3.0$ – 10.0 , $\Delta r = 1.0$ – 2.4); dotted-CPA at pH = 12.5 (k^2 , $\Delta k = 3.0$ – 8.6 ; $\Delta r = 1.0$ – 2.4); (b) magnitude of the Fourier transform for Pt co-ordination sphere: solid-CPA at pH = 1.5 HCl (k^2 , $\Delta k = 3.0$ – 10.7 ; $\Delta r = 1.0$ – 2.7 ; fit, 6.0 Pt–Cl); dashed-CPA at pH = 2.7 (k^2 , $\Delta k = 3.0$ – 10.0 ; $\Delta r = 1.0$ – 2.4 ; fit 2.8 Pt–Cl and 3.2 Pt–O); dotted-CPA at pH = 12.5 (k^2 , $\Delta k = 3.0$ – 8.6 ; $\Delta r = 1.0$ – 2.4 ; 1.8 Pt–Cl and 4.2 Pt–O).

1.8 Pt–Cl and 4.2 Pt–O bonds. At its natural pH, the calculated average co-ordination is 2.7 Cl[−] and 3.3 OH[−] or H₂O ligands. From EXAFS it is not possible to distinguish between Pt–OH and Pt–OH₂ ligands.

The initial pHs of solutions containing increasing amounts of CPA from 200 to 2000 ppm, 0.001 and 0.01 mol/l, respectively, are given in Table 1. As the Pt concentration increases, the pH decreases. The calculated pH assuming 2 H⁺/Pt is also listed in Table 1. The agreement between the measured and calculated pH indicates that CPA is a strong acid with the protons fully dissociated in aqueous solution in this pH range.

The Pt–Cl and Pt–O co-ordination numbers from the EXAFS fits for CPA at different concentrations are also given in Table 1. At a very low concentration of 30 ppm, a reddish-brown precipitate formed over the course of several months, similar to the observation of Miolati and Pardini [8]. EXAFS confirmed the composition of six Pt–O bonds in the precipitate. Fig. 4 shows that the Pt–Cl co-ordination number increases approximately linearly with increasing Pt concentration above 200 ppm. The figure also shows the Pt–Cl co-ordination of a 2400 ppm CPA solution determined by Pt NMR [14] and is in good agreement with these EXAFS determinations. The EXAFS and the previous Pt NMR data clearly show that the hexachloroplatinate(IV) dianion, PtCl₆^{2−}, is not usually present in dilute aqueous solutions of CPA. In Table 1 and Fig. 4, the Pt–Cl co-ordination number of the 200 ppm solution is about three. Under these moderately acidic conditions, dilute CPA solutions clearly undergo more extensive hydrolysis than predicted by most of the earlier hydrolysis models [1,3–5].

Fig. 5 shows the effect of pH, adjusted by addition of HNO₃ or NaOH, on the Pt co-ordination for 200, 1000 and 2000 ppm CPA (in all cases, “fresh/fresh” solutions). The natural pH of each concentration is

Table 1
Effect of CPA concentration on pH and EXAFS co-ordination numbers

Pt concentration (ppm)	pH measured	pH calculated	Pt–Cl co-ordination number	Pt–O co-ordination number
200	2.68	2.70	2.8	3.2
500	2.29	2.30	3.8	2.2
1000	2.01	2.00	4.0	2.0
1500	1.92	1.82	4.5	1.5
2000	1.75	1.69	4.8	1.2

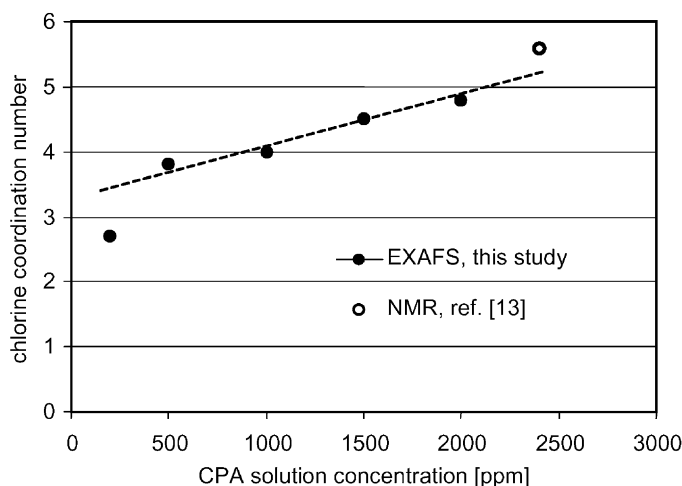


Fig. 4. Pt–Cl co-ordination numbers in CPA solutions at their natural pH as a function of CPA concentration.

indicated by an open symbol. At all Pt levels, the effect of increasing the pH (i.e. higher hydroxide concentration) is to increase the Pt–O co-ordination. For example, 200 ppm CPA solution at a pH of 1.5 has about 4.5 Pt–Cl bonds (and 1.5 Pt–O bonds). However, at a pH of about 9, there are two Pt–Cl bonds. As the Pt concentration increases, the Pt–Cl co-ordination number increases at a constant pH, indicating that more than the hydroxide ion/proton concentration affects the co-ordination sphere. Also shown in Fig. 5 is the Pt–Cl co-ordination number at a pH of 1.5 adjusted by

addition of HCl rather than HNO₃. At all Pt concentrations in HCl, there are six Pt–Cl bonds (i.e. PtCl₆²⁻).

The effect of excess chloride ion (added as NaCl) on the Pt co-ordination sphere of a 200 ppm CPA solution is shown in Fig. 6a. The dashed lines in this figure represent the fresh/fresh solutions. Addition of 0.05 M NaCl, which corresponds to a NaCl/CPA molar ratio of 50, or about an eight-fold increase in the amount of total Cl from CPA, leads to an increase in the Pt–Cl co-ordination number at all pH values. Below the natural pH (about 2.7), there are six Pt–Cl

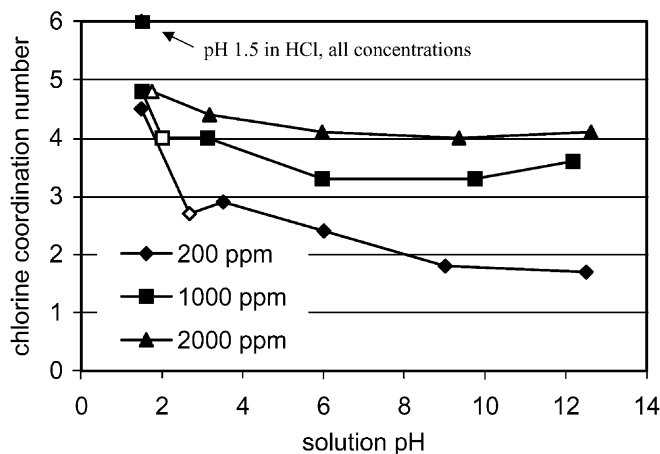


Fig. 5. Pt–Cl co-ordination numbers in freshly prepared 200, 1000, and 2000 ppm CPA solutions as a function of pH, acidified with HNO₃ or HCl where indicated, and basified with NaOH. The open symbols represent the natural pH.

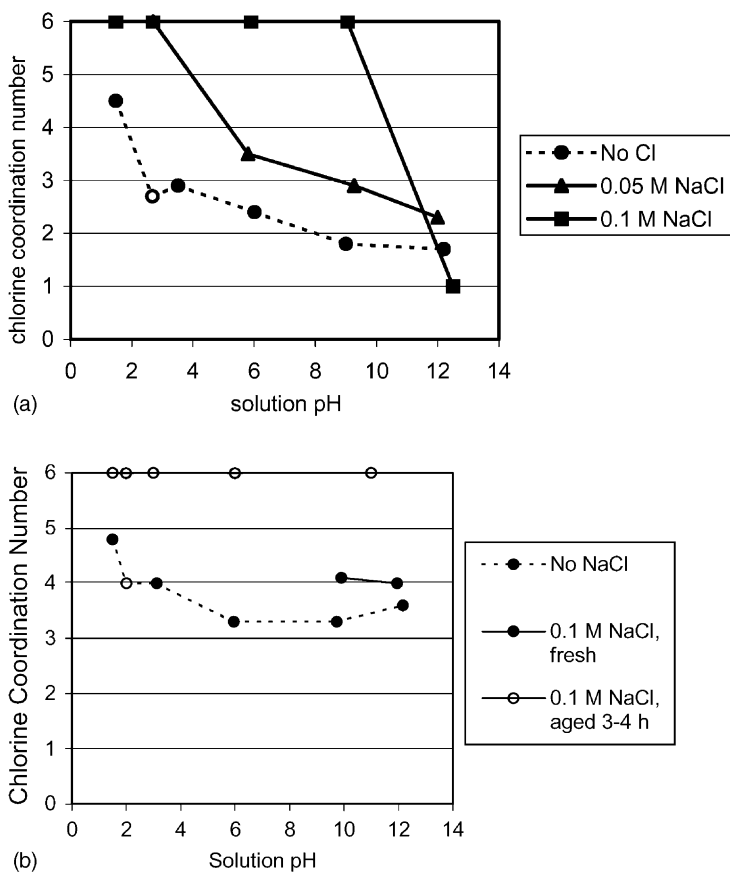


Fig. 6. The effect of chloride concentration (added as NaCl) on the Pt–Cl co-ordination numbers as a function of pH for: (a) 200 ppm solutions; (b) 1000 ppm solutions.

ligands. At higher pHs, the Pt–O co-ordination number increases. With a further increase to 0.1 M NaCl, PtCl_6^{2-} is present over a wide pH range up to about 9. In highly basic solutions ($\text{pH} = 12.5$), however, extensive hydrolysis occurs even at high Cl^- ion concentrations.

The trend of increasing Pt–Cl co-ordination number with added Cl^- ion concentration is similar for 1000 ppm CPA solutions, as seen in Fig. 6b. The addition of 0.1 M NaCl (NaCl/CPA molar ratio of 20) leads to only small immediate increases in Cl co-ordination, consistent with the 200 ppm solution of Fig. 6a for the 0.05 M NaCl solutions. The co-ordination spheres of 1000 ppm CPA solutions in 0.1 M NaCl which had been aged for 3–4 h, however, was fully chlorided up to pHs of about 11.

Except where noted above, each of the previous samples was analyzed within 1 h of preparation. Fig. 7 shows the effect of prolonged aging on the extent of CPA hydrolysis. Two aged pH series were compared to the fresh/fresh 200 ppm series (represented by circle symbols), the first is a fresh/aged series in which a fresh CPA solution at its natural pH of about 2.7 was adjusted to various pH values and then aged 2 weeks. Secondly, an aged/fresh series was prepared in which the CPA solution was itself aged (over the 2 weeks) where the initial pH decreased from about 2.7–2.4) before the pH was adjusted and analyzed by EXAFS.

After 2 weeks aging, the Pt–Cl co-ordination numbers in the fresh/aged series were lower than in the fresh/fresh series by about one Pt–Cl ligand, except at the most acidic pH (1.5). The Pt–Cl co-ordination

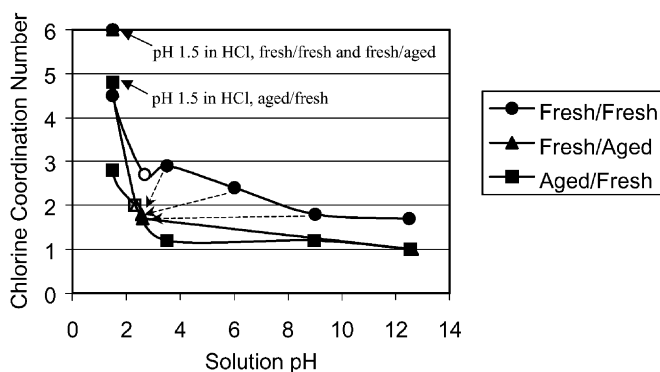


Fig. 7. The effect of aging on Pt–Cl co-ordination in 200 ppm CPA: fresh/fresh solutions (circles) were immediately analyzed after pH adjustment of freshly prepared CPA; fresh/aged solutions (triangles) were analyzed 2 weeks after pH adjustment of fresh CPA solutions; and aged/fresh solutions (squares) were immediately analyzed after pH adjustment of aged CPA.

number was about 1.5 for solutions with a pH greater than about 3, while the CPA aged at pH of 1.5 still contained about 4.5 Pt–Cl bonds, which is similar to the co-ordination geometry of fresh CPA under these conditions. It is clear that while significant hydrolysis occurs during the first hour, further reactions occur at longer times. Furthermore, this slow hydrolysis does not occur, or is significantly slower in strongly acidic solutions. Also included in these series are points for CPA aged in HCl at pH 1.5, under these conditions the CPA does not undergo hydrolysis, that is, Pt begins as PtCl_6^{2-} (Figs. 5 and 7) and is still PtCl_6^{2-} after 2 weeks.

Accompanying the additional ligand exchange, the pHs of the fresh/aged solutions dramatically decrease over the 2 weeks. These shifts are indicated by dashed arrows in Fig. 7. CPA decreases from an initial pH of 2.7 (represented by open circle) to 2.4, while solutions at pHs of 3.3, 6, and 9 all decreased to about 2.6. These reductions in pH will be discussed in more detail below.

Increasing the pH in the aged/fresh series (by addition of NaOH) results in a decrease of approximately one to two Pt–Cl ligands (Fig. 7, represented by squares) compared to the fresh/fresh species at the same pH. The complexes appear to contain approximately one Pt–Cl ligand for all pH values above the natural (aged) pH. With a decrease in pH by addition of HNO_3 (i.e. aged/aged CPA at a pH of 1.5) the number of Pt–Cl bonds increases to about three, but is significantly lower than that of fresh/fresh or fresh/aged

CPA (4.5 at a pH of 1.5). Addition of HCl (pH of 1.5) to the aged CPA in lieu of HNO_3 leads to further increase in the number of Pt–Cl ligands to about 4.8 in 1 h, however, under similar conditions fresh CPA becomes PtCl_6^{2-} (fresh/aged and fresh/fresh series in Fig. 7). After 2 weeks, the Pt–Cl co-ordination number of the aged CPA in pH 1.5 HCl further increased to six. In a similar experiment, a 200 ppm CPA solution initially at pH 2.68 was aged until its pH was 2.46 (not quite equilibrium). Upon addition of 0.05 M NaCl, the pH increased to its original value (pH of 2.7) in 4 days. These results indicate that unlike the Pt–O ligands which form in fresh CPA solutions, the Pt–O ligands which are formed by aging and lead to a drop in the pH are reversibly but not rapidly exchanged, by changes in pH or Cl^- ion concentration.

As seen in Fig. 7, the mid-pH solutions all converged to a pH close to 2.6 upon aging. Additional NaOH was added to several of these samples, in repeated small increments over the course of several months, in order to explore a “final” pH range above 2.6. Samples with final pH values of about 2.8 and 3.4 were obtained, from measured pH shifts and titration data, proton evolution was estimated to be about 3.5 and 4.0 H^+/Pt , respectively, while EXAFS revealed the presence of about 1.2 Cl^- and 4.8 O ligands in both samples.

The pH shifts in 200 ppm CPA solutions exposed to room light or maintained in the dark are shown in detail in Fig. 8. The shift in the natural pH of the 200 ppm CPA solution from 2.68 to 2.40 is seen as the

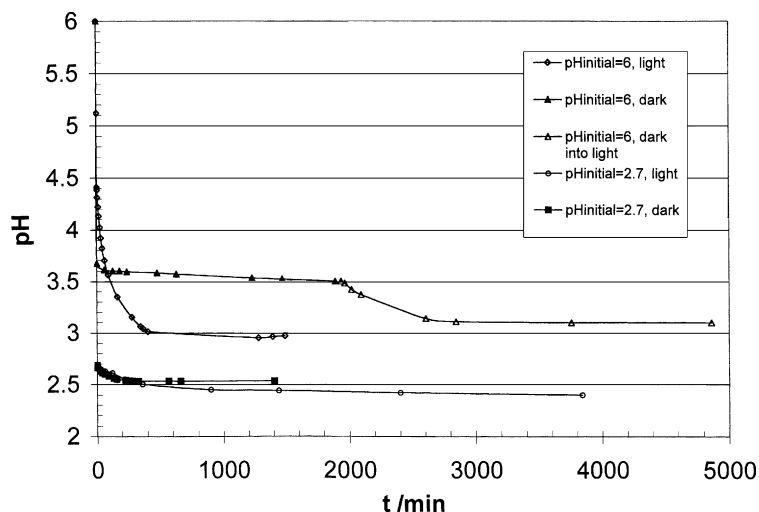


Fig. 8. Changes in pH vs. time for CPA solutions maintained in the dark and exposed to laboratory light.

lower set of open circles. The final pH corresponds to the evolution of about 2.0 protons per Pt atom. Successive runs came to within 10% of this value. If the experiment was conducted in 0.1 M Cl^- , no pH shift occurred outside of experimental error. Both of these observations are consistent with the data in Fig. 6, which indicates the presence of six Cl^- ligands when 200 ppm CPA at its natural pH is in 0.05 or 0.1 M excess Cl^- ion.

Another 200 ppm CPA solution was prepared with a basic NaOH solution such that the theoretical initial pH, assuming complete dissociation of the CPA, was 6.0. The pH of this sample (Fig. 8, represented by open diamonds) shifted down to a value of about 2.9 in the space of 24 h. After 2 weeks, the final pH of moderate initial pH solutions (Fig. 7) was generally observed to be about 2.6, corresponding to a released proton/Pt ratio of about 2.4 beyond the dissociation of CPA.

The influence of light is also shown in Fig. 8. At both pH values, the drop in pH is initially more rapid in the darkness, but it does not fall as far as the light-exposed sample. For the high-initial-pH, dark sample (represented by the filled in triangles in Fig. 8) the proton release to a pH of about 3.5 corresponds only to about 0.31 H^+/Pt . When the high-pH dark sample was exposed to light (represented by open triangles in Fig. 8), the pH dropped significantly and approached the values of the solutions continuously aged

in the presence of visible light. The pH decrease of the low pH dark sample (represented by filled squares) corresponds to a H^+ released/Pt ratio of 1.0, compared to a value of 2.0 H^+/Pt for the sample exposed to room lighting.

EXAFS co-ordination numbers for the CPA solutions aged in the light and dark are shown in Table 2. For fresh CPA solutions, exposure to laboratory light has little influence on the Pt co-ordination. Thus, the initial hydrolysis of CPA is not affected by light. For CPA solutions aged for 2 weeks in the dark, there is little change, while for the same solution aged in the light, the Pt–Cl co-ordination number decreases slightly to about two (with four Pt–O ligands). Thus, the approximate average ligand composition of the fresh CPA species at concentrations and pHs often used for preparation of catalysts is $[\text{PtCl}_3\text{O}_3]$, while that of the aged solutions is $[\text{PtCl}_2\text{O}_4]$.

Table 2
Effect of visible light on Pt co-ordination numbers 200 ppm CPA

Time	Visible light	Pt–Cl	Pt–O
1 h	Yes	2.5	3.5
1 h	No	2.7	3.3
2 weeks	Yes	2.1	3.9
2 weeks	No	2.8	3.2

At a higher CPA concentration of 500 ppm, which started with an initial pH of 2.28 (theoretical value assuming complete dissociation: 2.29, Table 1), a downward shift in pH equilibrated at 2.19, which corresponds to only 0.2 protons released per Pt. At 1000 ppm, CPA was completely stable at its initial natural pH, 2.00 (Table 1). In the discussion below the slow, late drops in pH will be taken as hydroxide exchange for water ligands. Fig. 4 shows that the 500 and 1000 ppm solutions contain only four chloride ligands, apparently the other two ligands are water, and no hydroxide ion ligand exchanged for them.

4. Discussion

4.1. CPA hydrolysis pathway

There are essentially three CPA speciation models found in the literature, those of Miolati and Pardini [8], Sillen and Martell [1], and Knözinger and co-workers [3]. The pathway of Miolati and Pardini [8] assumes that only hydroxide ions exchange for chloride ions (Eq. (1)), thus, no aquo complexes are possible. This mechanism has several shortcomings. First, it fails to predict the formation of both types of Pt–O ligands, that is, aquo and hydroxide ion ligands. Consequently, the pathway cannot account for ligands undergoing substitution at very different rates or for the charge on the Pt complexes being anything but -2 . In contrast, the present findings suggest that under many solution conditions, there are a significant number of aquo ligands resulting in Pt complexes with charges other than -2 . For example, in a 200 ppm CPA solution the initial pH is 2.68 (Table 1), which is due to only the dissociation of the strong acid. Based on this pH measurement and Eq. (1), the initial CPA solution species would not be expected to contain any Pt–OH bonds. EXAFS analysis, however, indicates that there are about 3.5 Pt–O and 2.5 Pt–Cl bonds (Figs. 4–7). If Cl ligands were exchanged only by hydroxide ions by the Miolati and Pardini pathway [8], the pH would have decreased to about 2.25 and no long-term drop in pH would occur. Figs. 7 and 8 show that the middle to basic pH drift is quite significant. These extreme pH shifts during aging have been corroborated elsewhere [13]. The initial rapid hydrolysis of Pt–Cl bonds

evidenced by EXAFS, therefore, appears to be due to ligand exchange by H_2O leading to Pt–O co-ordination without a change in pH. The observed decrease in pH is postulated to occur as hydroxide ligands form in a subsequent and slow process.

Furthermore, the charge of species containing aquo ligands must not be -2 ; in the discussion below, an estimation of the complex composition will be made using the EXAFS data for chloride co-ordination, and the potentiometric data for the hydroxide ligand co-ordination. The equilibrium complex stemming from 200 ppm CPA at a pH of about 2.4 appears to be $[\text{PtCl}_2(\text{OH})_2(\text{H}_2\text{O})_2]^0$, for example, and zero valent species are abundant in excess chloride in the mid-pH range. Thus, it appears that under both acidic and basic conditions the initial Pt–O bonds are due to co-ordinated H_2O , and zero valent species are abundant at equilibrium; the Miolati and Pardini mechanism [8] appears incorrect in these aspects.

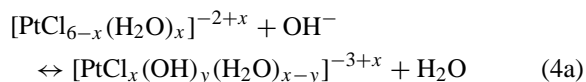
The second speciation pathway, of Knözinger and co-workers [3], proposes that CPA is a weak acid, not fully dissociated. In addition, only two chloride ligands may be substituted by either aquo or hydroxide ion ligands. The results of the present study suggest that this pathway is also incorrect or inapplicable at dilute concentration. First, the initial pH values shown in Table 1 agree closely with the calculated values assuming that H_2PtCl_6 is a strong acid, i.e. fully dissociated in aqueous solution at concentrations below 2000 ppm. Only at pH values approaching 1, or concentrations of 0.1 M (20,000 ppm), does CPA appear to remain partially undissociated [14]. Furthermore the pathway fails to predict substitution of more than two Cl ligands in low concentration CPA solutions. Knözinger and co-workers [3] used CPA solutions of initial concentration 5×10^{-3} M (about 1000 ppm). At 1000 ppm CPA, Figs. 4 and 5 reveals that while the chloride co-ordination number is at or above 4 for acidic pH values, it drops to near 3 in the mid-pH range. Many of the solutions they studied, in contact with alumina, terminated in this mid-pH range [3] due to the consumption of protons as the hydroxyl groups at the alumina surface become charged [7].

The pathway of Sillen and Martell [1] (Eqs. (2) and shown in Fig. 1) does assume that CPA is a strong acid but also restricts the chloride ligand exchange to two. This may well have been acceptable with the

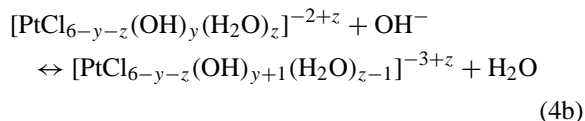
concentrated solutions and the low pH range employed in earlier studies. Lambert and co-workers, while fitting it with different formation and dissociation constants and adding the *cis* and *trans* tetrachloro isomers, largely keeps to this pathway [13]. They studied relatively high concentrations of 1.2 and 6.6×10^{-2} M, or 2400 and 13,200 ppm. They also saw large, slow (1–2 days) downward shifts in pH and observed that the ^{195}Pt NMR chemical shift of the Pt complexes with oxygen ligands drifted to lower values during aging, while the chemical shift of PtCl_6^{2-} did not change. Their interpretation of the NMR results was consistent with the Sillen and Martell mechanism: the slow decrease in pH is brought about by the slow, rate-limiting hydrolysis reactions (Eq. (2)), followed by rapid deprotonation (Eq. (3)).

The present interpretation is contrary to these mechanistic details of the Sillen and Martell pathway. As mentioned above, the current EXAFS results obtained at short times (30 min) reveal that hydrolysis occurs quickly, without a change in pH, and a “late” pH shift is attributed to slow co-ordination of hydroxide ligands. This is most clearly seen in the case of the aging of the fresh/fresh 200 ppm solution initially at pH 9 (circle symbol, Fig. 7). The chloride co-ordination number, about two, remains practically constant during aging and the final pH of the solution, about 2.6 corresponds to the loss of about two protons per Pt complex. The average composition of the Pt complexes at the final pH of 2.6 is then approximately $[\text{PtCl}_2(\text{OH})_2(\text{H}_2\text{O})]_0^0$ and must have started at pH 9 as $[\text{PtCl}_2(\text{H}_2\text{O})_4]^{2+}$. Thus, in the present work the exchange of water with OH ligands is clearly a slow process. The fresh/fresh solutions at pHs 3 and 6 also lose one chloride in addition to gaining two hydroxide ligands during aging.

The reaction which leads to an increase in the proton concentration may be either the dissociation of a weak acid or ligand exchange of hydroxide for water. That the rate of this reaction is slow suggests that it is the slower substitution reaction, not deprotonation, which normally occurs very fast. Thus, a hydroxide-water exchange as written in Eq. (4) should replace the dissociation reactions of Eq. (3):



or, written more generally for chloroaquohydroxo complexes,



The substitution reaction of Eq. (4) can also explain the acceleration of proton accumulation in light, as seen in Fig. 8. While acid dissociation reactions are not normally thought to be light sensitive, ligand exchange can be.

A number of comments may be made to rectify the recent work of Lambert and co-workers [13] to the present study. In their work, pH shifts from 10.9 to 3.0 were observed in 1.2×10^{-2} M CPA solutions in 1–2 days. While this shift is quite dramatic, the solution concentration they employ is relatively high; the change in proton concentration corresponds to approximately 0.2 H^+ /Pt. The overall extent of hydrolysis during the aging process was small and would have been difficult to quantify with NMR. The sampling times with NMR of up to 12 h were relatively long. At these experimental conditions, it would be very difficult to delineate between slow and rapid hydrolysis and dissociation/OH exchange processes. With the low concentration of CPA employed in the present study, high degrees of hydrolysis were observed, and the rapid EXAFS acquisition permitted such delineation.

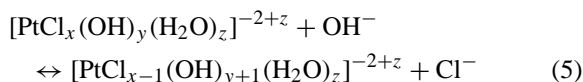
In their analysis of NMR shifts, they assumed the rapid deprotonation of aquo complexes [13], following the earlier postulation of Barton et al. [21]. The downward shift in pH was assumed to arise from slow (rate determining) hydrolysis followed by immediate deprotonation. Correspondingly, NMR peaks of penta and tetrachloro complexes at higher chemical shifts (about a 660 ppm shift for the pentachloride and a 1270 ppm shift for the tetrachloride) in the high pH range were assigned to hydroxo complexes and in the aged solutions at low pH the analogous NMR peaks at lower chemical shifts were assigned to the aquo complexes (about a 500 ppm shift for the pentachloride and a 1000 ppm shift for the tetrachloride).

The present results would suggest exactly the opposite assignment: the initial ligands at high pH would be the aquo ligands, while those after aging and the production of protons would be the hydroxo ligands. At least in dilute CPA solutions, proton exchange between

the aquo and hydroxo complexes is slow. Perhaps there is a drastic change in the mechanism as Pt concentration increases, however, some aspects of the NMR data at high Pt concentration [13] call into question the assumption that hydrolysis is slow. If so, a fresh spectrum would be expected to reflect high amounts of $[\text{PtCl}_6]^{2-}$ and almost no penta or tetrachloride signals, and these peaks should increase over time. In the data [13], it appears that large amounts of the pentachloride and tetrachloride are present in the fresh solutions, and no clear increase in signals from these species is seen in the aged samples.

Up to this point the general pathway of Sillen and Martell appears to be valid in several aspects, excepting some differences in the mechanistic detail. First, the hydrolysis reactions, Eq. (2), need not be assumed slow, and second, the formation of OH ligands should be changed from rapid weak acid dissociation, Eq. (3), to slow water–OH exchange, Eq. (4). However, the water–chloride exchange reactions, Eq. (2), and the OH–water exchange reactions, Eq. (4), are yet insufficient to explain some of the present observations. If the speciation mechanism comprises only these two reactions, two trends are predicted: first, in excess chloride, pH should not be dependent on hydrolysis, per Eq. (2). In Fig. 6a, precisely this dependence is seen in the 200 ppm CPA sample in 0.05 M NaCl. The higher concentration (Fig. 6b) exhibits weak but discernable pH dependence. Second, from Eq. (4), chloride concentration should have no effect once the OH ligands form. In fact, adding chloride to an aged CPA solution

did slowly raise the pH back to the initial value as the hexachloride complex reformed. Both of these trends indicate that chloride exchange for OH occurs. This behavior can be modeled by the Miolati and Pendini mechanism [8] if it is altered slightly to account for OH exchange in aquo complexes, as shown in Eq. (5) below.



Finally, the Sillen and Martell pathway does not account for the more extensive hydrolysis, which occurs at lower CPA concentrations and at high pH. In the most general speciation scheme, CPA hydrolysis is qualitatively described by Eqs. (2), (4) and (5), where the degree of chloride exchange can vary from 0–6 depending on the CPA concentration, pH, chloride ion concentration and time.

4.2. Aqueous Pt (IV) species from CPA

Fig. 9 shows all the possible octahedral Pt (IV) co-ordination complexes with chloride, aquo, and hydroxide ligands (excepting isomers, for simplicity). In Fig. 9a horizontal movement represents a ligand exchange between chloride and water (Eq. (2)), a vertical movement represents an exchange between water and hydroxide ion (Eq. (4)), and a diagonal movement represents an exchange between chloride and hydroxide ion (Eq. (5)). While Fig. 9 lists all of the possible

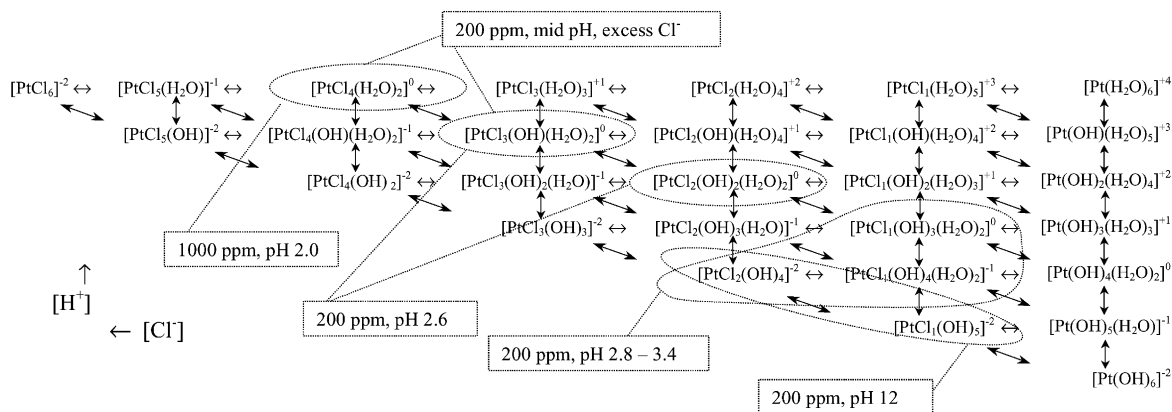


Fig. 9. A comprehensive speciation pathway for CPA.

Pt complexes, all are not equally probable: the CPA concentration, pH, chloride concentration, and age of the solution determine the dominant species. At low pH, high CPA and high Cl concentration, high co-ordination of Cl is favored, (see the upper right corner of Fig. 9). Since, high chloride and proton concentrations also limit hydroxide ion exchange, the predominant Pt–O species are due to aquo ligands. Depending on the exact solution composition, there may be no exchange of Pt–Cl bonds, i.e. PtCl_6^{2-} , while at lower CPA concentrations at pHs from about 2.5 to 9 and in the absence of excess Cl^- ion, there may be up to about 3–4 Pt–OH₂ bonds. Furthermore, since hydroxide ligand exchange is relatively slow, the initial Pt(IV) complexes likely contain few Pt–OH ligands.

The estimated composition of a number of Pt species at various conditions of this work are shown in Table 3 and are highlighted in Fig. 9. The Pt–Cl and total Pt–O co-ordination numbers were obtained by EXAFS. In addition, the number of Pt–OH ligands can be estimated from pH measurements. The H^+ evolved from OH–H₂O exchange equals the proton ion concentration minus two times the Pt concentration (since CPA is a strong diprotic acid). The concentration of protons evolved divided by the Pt concentration gives the number of Pt–OH ligands. The number of aquo ligands can finally be calculated from the difference in the total Pt–O co-ordination number and the number of Pt–OH bonds. For example, for a fresh 200 ppm CPA solutions, EXAFS indicates there are about three Pt–Cl ($N = 2.8$) and three Pt–O ligands ($N = 3.2$). Within the first hour, the pH is 2.68 and the number of protons is due entirely to the strongly acid protons. Thus, there are no Pt–OH ligands and the average Pt species is approximately $[\text{PtCl}_3(\text{H}_2\text{O})_3]^{1+}$. After

aging, the final pH decreases to 2.4 and is equivalent to about 2.0 protons per Pt, i.e. 2 Pt–OH ligands. In addition, EXAFS indicates that the Pt–Cl and Pt–O co-ordination numbers are 2.1 and 3.9, respectively. The average Pt species of the aged, 200 ppm CPA solutions at pH 2.40 is $[\text{PtCl}_2(\text{OH})_2(\text{H}_2\text{O})_2]^0$.

At moderately basic conditions, 200 ppm CPA at an initial pH of 9 (Table 3, third row), for example, the final pH shift to around 2.6 (Fig. 7) corresponds to about 2.4 Pt–OH. Also from Fig. 7, the EXAFS Pt–Cl co-ordination number is approximately 1.8. If there is a narrow distribution of species, then approximately 80–90% of the Pt in this aged solution is present as $[\text{PtCl}_2(\text{OH})_2(\text{H}_2\text{O})_2]^0$ and 10–20% as $[\text{PtCl}_1(\text{OH})_3(\text{H}_2\text{O})_2]^0$. Above a pH of 2.6, in the range 2.8–3.4, the composition of the two solutions investigated might be a mixture of $[\text{PtCl}_1(\text{OH})_3(\text{H}_2\text{O})_2]^0$, $[\text{PtCl}_1(\text{OH})_4(\text{H}_2\text{O})]^{1-}$ and $[\text{PtCl}_2(\text{OH})_4]^{2-}$.

At higher CPA concentrations, neutral species are again predicted for 500 and 1000 ppm solutions at their natural pH. At 500 ppm CPA, there is only a small decrease in the pH, from 2.28 to 2.19, which is equivalent to about 0.2 OH⁻/Pt. Thus, at 500 ppm CPA there are few Pt–OH ligands even in aged solutions. The EXAFS Pt–Cl co-ordination number is 3.8 suggesting that the average Pt co-ordination is $[\text{PtCl}_4(\text{H}_2\text{O})_2]^0$, with perhaps a small amount of $[\text{PtCl}_3(\text{OH})(\text{H}_2\text{O})_2]^0$. At 1000 ppm CPA the only change in the pH is caused by the strongly acidic protons. Thus, there are no Pt–OH ligands. With an EXAFS Pt–Cl co-ordination number of 4.0, the dominant species is $[\text{PtCl}_4(\text{H}_2\text{O})_2]^0$.

Tables 3 and 4 also show that in the presence of excess chloride ion, many of the Pt complexes are also neutrally valent. For example, for a 200 ppm CPA solution in 0.05 M NaCl at a pH of 5.8, the pH decreased

Table 3
Calculation of complex composition

CPA concentration (ppm)	pH	H^+ release (OH) _x	EXAFS Cl ⁻ CN	Estimated species
200	2.68 (initial)	0	3	$[\text{PtCl}_3(\text{H}_2\text{O})_3]^{1+}$
200	2.40 (final)	2	2	$[\text{PtCl}_2(\text{OH})_2(\text{H}_2\text{O})_2]^0$
200	6.07 → 2.60, 9.10 → 2.61	2.4	1.7–1.8	$[\text{PtCl}_2(\text{OH})_2(\text{H}_2\text{O})_2]^0$, $[\text{PtCl}_1(\text{OH})_3(\text{H}_2\text{O})_2]^0$
500	2.28 → 2.19	0.2	3.8	$[\text{PtCl}_3(\text{OH})(\text{H}_2\text{O})_2]^0$, $[\text{PtCl}_4(\text{H}_2\text{O})_2]^0$
1000	2.00	0	4	$[\text{PtCl}_4(\text{H}_2\text{O})_2]^0$
200, 0.05 M NaCl	9.27 → 7.84	0.9	3.0	$[\text{PtCl}_3(\text{OH})(\text{H}_2\text{O})_2]^0$
200, 0.05 M NaCl	5.80 → 5.20	0.1	3.5	$[\text{PtCl}_4(\text{H}_2\text{O})_2]^0$, $[\text{PtCl}_3(\text{OH})(\text{H}_2\text{O})_2]^0$
200, 0.05 M NaCl	12.00 → 11.78	4.0	2.2	$[\text{PtCl}_2(\text{OH})_4]^{2-}$

Table 4
Reversibility of pH shifts in excess Cl⁻

	Acidified		Basified				
	HCl	HNO ₃	Natural	NaOH	NaOH	NaOH	NaOH
Initial pH shift	1.50 → 1.38	1.50 → 1.30	2.68 → 2.46	3.51 → 2.54	6.01 → 2.61	9.01 → 2.60	12.20 → 12.21
pH shift after addition of 0.05 M NaCl							
30 min	1.40	1.32	2.50	2.58	2.66	2.64	12.16
2 h	1.41	1.32	2.52	2.58	2.68	2.65	12.19
16 h	1.46	1.38	2.63	2.66	2.80	2.76	12.20
4 days	1.48	1.34	2.67	2.68	2.82	2.78	12.19

to 5.2 upon aging, equivalent to about 0.1 Pt–OH/Pt. Unlike the acidic CPA solutions, the pH shifts in neutral to basic solutions were rapid. The number of protons due to hydroxide co-ordination was determined from the pH after accounting for titration of the two acidic protons. EXAFS analysis of aged 200 ppm CPA at a pH of 5.2 and in 0.05 M NaCl indicates that there are about 3.5 Pt–Cl and 2.5 Pt–O bonds. Thus, the number of [PtCl₄(H₂O)₂]⁰ and [PtCl₃(H₂O)₃]¹⁺ species are about equal; approximately 10% of them have one aquo ligand substituted by hydroxide ligands. Increasing the final pH to 7.8 decreases the number of Pt–Cl ligands and increases the number of Pt–OH ligands. At this slightly basic pH, the average species is [PtCl₃(OH)(H₂O)₂]⁰. Increasing the final pH further to 11.8 leads to a decrease in the Pt–Cl co-ordination number and a further increase in the number of Pt–OH ligands. Under these strongly basic conditions, few aquo ligands remain, and the charge on the Pt complexes becomes negative. The average species becomes [PtCl₂(OH)₄]²⁻. It is interesting to note that in the absence of excess chloride, the final pH of 200 ppm CPA solutions at an initial pH from about 3.3 to 9 decreases to about 2.6, while the decrease in pH of similar solutions in 0.05 NaCl is much less. As previously discussed, excess chloride limits the degree of hydroxide ligand exchange.

With increasing time and hydroxide ion concentration, the number of Pt–OH ligands increases and the number of Pt–Cl bonds decreases. Typical solution species of aged CPA solutions at moderate to highly basic pH are circled in Fig. 9. In general, aged solutions at moderate to high pH contain varying amounts of chloride, aquo and hydroxide ligands.

For these 200–2000 ppm CPA solutions, there appear to be three to five Pt–OH ligands at the most basic conditions, and the Pt probably still contains at least one to two Pt–Cl bonds. At the 200 ppm concentration, the charge of species appears to change rapidly above a pH of 2.6. Since, chloride ions inhibit hydroxide ion co-ordination, Eq. (5), and CPA contains six chlorine ligands/Pt, complete hydroxide exchange with precipitation of H₂Pt(OH)₆ (or Na₂Pt(OH)₆ under basic conditions) occurs only when the CPA and chloride concentrations are low. Apparently, at higher CPA concentrations the chloride concentration is sufficiently high to inhibit complete hydroxide ion ligand exchange. Thus, higher concentrations of CPA are stable to precipitation even at high pH.

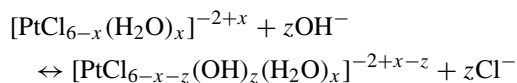
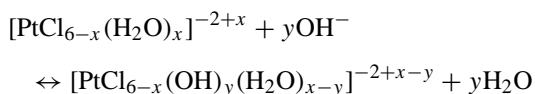
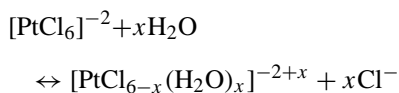
The Pt co-ordination complexes expected from the Miolati hydrolysis pathway are along the bottom diagonal in Fig. 9. They generally do not overlap with the shaded areas. While the co-ordination pathway predicted by Miolati does not agree with the observed species obtained by dissolving CPA in aqueous solution, in principle it is possible to manipulate the conditions to obtain these species. For example, if a 200 ppm CPA solution at its natural pH were aged for 24 h, the predominant species would be PtCl₂(H₂O)₂(OH)₂. Addition of 0.05–0.1 M NaCl would quickly lead to PtCl₄(OH)₂, since, ligand substitution of aquo and chloride ligands is rapid. Of course, at longer times the hydroxide ions would be replaced by chloride ligands as well. Nevertheless, a Pt complex with only chloro and hydroxide ligands would temporarily be present. Following a similar procedure with either lower CPA concentrations or a much higher pH, the remaining complexes predicted by the Miolati pathway could also be obtained.

The Pt co-ordination pathway of Sillen and Martell pathway is seen as the three left-most columns, if the diagonal arrows are excluded. While all of these species probably exist in solution at some conditions, at low pH, high CPA and chloride concentration where these species dominate, the relative concentration of Pt species with hydroxide ligands is likely quite small. Both low pH and high chloride concentration limit the extent of hydroxide ligand exchange, therefore, it is likely that under these conditions aquo ligands dominate CPA hydrolysis.

Since CPA is one of the most often used Pt salts for preparing supported catalysts, this study investigated the effect of the solution conditions on the nature of the Pt species. In addition, since catalytic supports often alter the pH of the impregnating solution, the effect of the pH on the CPA solutions should provide some insight as to the possible Pt species present during adsorption onto the support. The adsorption of CPA onto alumina and the changes in ligand composition will be reported in a later paper [18].

5. Conclusions

The APS permitted EXAFS characterization of the hydrolysis chemistry of dilute CPA solutions. Hydrogen hexachloroplatinate(IV) is a strong acid, which undergoes rapid and extensive hydrolysis. In dilute acidic solutions, the degree of hydrolysis is much higher than has previously been reported at higher concentrations. The previous speciation pathways are shown to be incorrect or incomplete. From a comparison of potentiometric data and EXAFS analysis of the co-ordination shell, a series of three reactions is proposed to account for all the hydrolysis products at different CPA concentrations, pHs, chloride ion concentrations and times. Writing only the aquo complexes, and not the aquohydroxo complexes on the left-hand side for clarity, this set of reactions is as follows:



The initial hydrolysis reaction, aquo ligand exchange of chloride ions, is rapid and reversible; while the latter two reactions, hydroxide ion ligand exchange of chloride and aquo ligands, are relatively slow, at least in acidic solutions. In addition, the rate of the latter two reactions is accelerated in the presence of light. Many of the stable Pt complexes in solution are zero valent. High chloride co-ordination is favored at low pH and high chloride concentration. As a result, the $[\text{PtCl}_6]^{2-}$ species is present only in acidic solutions and with a moderate excess of chloride ion or in the neutral solutions with a large excess of chloride ion. Hydroxide ligand formation is favored at low pH and suppressed by chloride ion concentration. As a result, full hydrolysis of CPA by hydroxide ions with precipitation of $\text{H}_2\text{Pt}(\text{OH})_6$ (or $\text{Na}_2\text{Pt}(\text{OH})_6$) is favored only at very low CPA concentrations (ca. 30 ppm).

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