

Application of NMR to Interfacial Coordination Chemistry: A ^{195}Pt NMR Study of the Interaction of Hexachloroplatinic Acid Aqueous Solutions with Alumina

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Abstract: To understand the mechanism of Pt deposition during the synthesis of supported catalysts, liquid-phase ^{195}Pt NMR spectroscopy was applied first to study the speciation of platinum complexes in aqueous solutions of H_2PtCl_6 as a function of pH and time of hydrolysis and second to follow the adsorption of platinum complexes on γ -alumina from these solutions. Five of the six Pt complexes that can exist in hydrolyzed H_2PtCl_6 solutions are identified by their ^{195}Pt chemical shift (δ_{Pt}): $[\text{PtCl}_6]^{2-}$, $[\text{PtCl}_5(\text{H}_2\text{O})]^-$, $[\text{PtCl}_5(\text{OH})]^{2-}$, $[\text{PtCl}_4(\text{H}_2\text{O})_2]$, and $[\text{PtCl}_4(\text{OH})_2]^{2-}$. For $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$, which cannot be directly detected in NMR spectra due to fast proton exchange, δ_{Pt} is calculated from the best fit of the $\delta_{\text{Pt}} = f(\text{pH})$ dependence to the experimental data. The acid dissociation constants ($\text{p}K_{\text{a}}$) for aquaplatinates are also determined and discussed in comparison to literature data. For H_2PtCl_6 solution– Al_2O_3 mixtures, NMR signals of $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{OH})]^{2-}$ at the interface were observed for the first time. The $[\text{PtCl}_6]^{2-}$ signal has a small negative δ_{Pt} relative to that in H_2PtCl_6 solutions, which indicates a slight perturbation of the Pt atom coordination sphere by the alumina surface. It is suggested that adsorbed $[\text{PtCl}_5(\text{OH})]^{2-}$ results from fast deprotonation of the water molecule ligand in $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ by alumina basic hydroxyls. Most likely, the platinum anions are held on the positively charged alumina surface by electrostatic interaction. The fraction of adsorbed $[\text{PtCl}_5(\text{OH})]^{2-}$ rises with increasing initial pH of H_2PtCl_6 solutions and becomes dominant at higher pH. The $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{OH})]^{2-}$ signals disappear after removal of physisorbed water from alumina powder at room temperature and reappear almost unchanged upon subsequent rewetting of the solid. In contrast, after drying at 90 °C for 1.5 h, no NMR signal can be detected for the dried samples, and much weaker signals than those in the original solid are observed for the rewetted sample. The disappearance of the NMR signals is supposed to be due to formation of lower symmetry grafted Pt complexes with a higher chemical shift anisotropy. The likely mechanisms of platinum deposition from acidic H_2PtCl_6 solutions on positively charged alumina surface are discussed.

Introduction

Studies on ion adsorption on inorganic oxides from aqueous solutions have been extensive in recent years owing to the importance of these systems, particularly, in catalyst manufacturing, heterogeneous catalysis, and material science.¹

This paper concerns Pt/ Al_2O_3 materials prepared by deposition from aqueous solutions of Pt precursors. Catalysts with well-dispersed Pt metal particles on high surface area oxide supports have received much attention because of their wide commercial application. The Pt/ Al_2O_3 system is of particular interest, since all modern industrial reforming catalysts consist of Pt, usually combined with one or more metals, deposited on a chlorinated alumina.²

Pt/ Al_2O_3 catalysts are routinely prepared by impregnation of an alumina support with an aqueous solution of a suitable platinum complex (typically, an H_2PtCl_6 solution) followed by drying, calcination, and reduction to yield Pt metal particles. Until presently, there has been very little definite information on the initial stages of Pt complex interaction with the alumina surface despite the fact that it may have a crucial effect on the distribution of Pt particle sizes and, consequently, on the performance of the final catalyst after its reductive treatment.

When alumina is brought into contact with an acidic aqueous solution of H_2PtCl_6 , the surface OH groups, which behave like a weak base, are protonated. At pH values lower than the point

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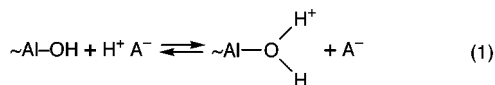
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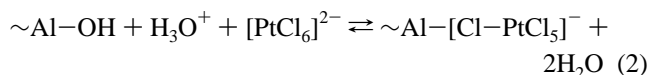
(2) Boitiaux, J. P.; Devès, J. M.; Didillon, B.; Marcilly, C. R. In *Catalytic Naphtha Reforming: Science and Technology*; Marcel Dekker: New York, 1994; pp 79–111.

of zero charge (PZC) of alumina (pH \approx 8), the surface is positively charged by protonation, and *electrostatic adsorption* of anionic platinum complexes on the positively charged surface hydroxyl groups can occur:^{2,3}



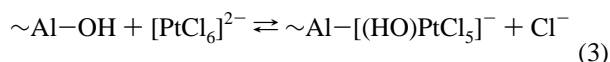
where A⁻ stands for anionic platinum complexes. Because of proton consumption, the pH of the solution increases as reaction 1 proceeds to an extent that depends on the Pt/alumina ratio.

Other mechanisms for the fixation of platinum on the alumina surface are also often considered. One of them, called *anion exchange*, is the exchange of surface OH groups with platinum anions:^{2,4}

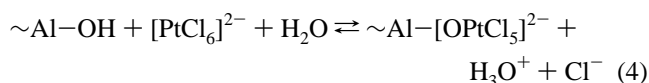


This reaction should also lead to an increase of pH; the adsorbed Pt complex may be considered to be grafted.

Another process, also called *ligand exchange*, may result in grafting. It consists of the replacement of one or two ligands in the *coordination sphere of platinum* by surface OH groups of alumina;²⁻⁴ for example, for [PtCl₆]²⁻, this process can be represented as follows:



Ligand exchange can be followed by deprotonation of the bridging OH group as proposed by Martens and Prins:⁵



The adsorption of H₂PtCl₆ on γ -Al₂O₃ from aqueous solutions under equilibrium conditions was studied in several papers.^{3,5,6} It was found that the amount of adsorbed Pt was strongly dependent on the pH of H₂PtCl₆ solutions and passed through a maximum at pH = 3.5–4 (measured in the final solution).^{3,6} No Pt adsorption was observed above a pH of 8.2, i.e., above the PZC of alumina. Mang et al.³ applied a modified triple-layer model to simulate the pH dependence of the Pt uptake. A rather satisfactory agreement between the experimental and simulated data was achieved when adsorption by ligand exchange of the chloroaqua and chlorohydroxo platinum anionic complexes with surface $\sim\text{Al}-\text{OH}$ and $\sim\text{Al}-\text{O}^-$ groups (reaction 3) was taken into account in addition to electrostatic fixation of the Pt anions (reaction 1). The latter process is dominant at pH < 4. At higher pH, the adsorption capacity decreases as the pH approaches the PZC of alumina, and simultaneously the ligand exchange mechanism becomes increasingly important. The decrease in the Pt uptake at pH < 4 is explained by competitive adsorption of Cl⁻ on positively charged surface sites. It was also noted that nonnegligible dissolution of alumina occurs at pH < 4.

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Summers and Ausen⁷ reported that the adsorption of (NH₄)₂-PtCl₆ on γ -alumina was accompanied by the release of free uncoordinated Cl⁻ ions into the solution and suggested that this effect points to a ligand exchange reaction occurring between Pt complexes and the support (reaction 3 or 4).

Probably, one of the main reasons for the poor understanding of the initial stages of platinum deposition on alumina is the lack of a spectroscopic technique suitable for detecting Pt speciation at the alumina–aqueous solution interface and sensitive enough to follow the modifications of the Pt ion coordination sphere occurring upon adsorption.

Several attempts have been made to identify the platinum complexes, which are fixed on the surface of alumina from H₂-PtCl₆ solutions, using diffuse reflectance UV–visible spectroscopy.^{3,8,9} A considerable shift of the charge-transfer (CT) band maxima relative to their position in solutions was found to occur in the spectra of H₂PtCl₆ adsorbed on γ -Al₂O₃, which is strongly indicative of a metal precursor–alumina support interaction. However, the reported maxima for the CT bands differ appreciably even for samples prepared by essentially the same procedure. Despite the considerable disagreement in the reported band positions, the observed CT bands were ascribed to adsorbed [PtCl₆]²⁻ or [PtCl₅(OH)]²⁻, which are supposed to be the major species. It should be underlined, however, that there is no agreement on assigning one or several bands at precise positions to a specific species.

Laser Raman experiments on γ -alumina impregnated with an acidic H₂PtCl₆ solution and dried at relatively low temperatures (20–120 °C)^{3,5,10} confirmed the conclusions drawn from UV–vis spectra. Three^{3,5} or five¹⁰ absorption bands were observed in the Raman spectra in the range 167 to 353 cm⁻¹, which correspond rather well to the literature data for [PtCl₆]²⁻ in the solid state and solutions. It was thus concluded that the adsorbed platinum basically consists of slightly distorted [PtCl₆]²⁻ species, some of which may be ligand exchanged. However, no specific information on the structures and compositions of the exchanged platinum complexes could be deduced from the Raman experiments.

To some extent, the Raman data were supported by the EXAFS study of dried uncalcined ex-H₂PtCl₆/Al₂O₃,¹¹ which indicated the presence of weakly bonded adsorbed [PtCl₅]²⁻ as a major species along with small amounts of Pt complexes whose coordination sphere contained oxygen atoms. However, in the later EXAFS work,¹² it was concluded that, at the drying stage, the platinum precursor interacts strongly with the support to form mainly PtCl₄(O₂).

Thus, as follows from the above brief survey, more effort is needed to gain a deeper insight into the mechanism of platinum complex deposition on alumina from aqueous solutions.

In this work, we attempted to apply static ¹⁹⁵Pt NMR spectroscopy to the study of platinum adsorption on γ -alumina from acidic H₂PtCl₆ solutions at different initial pH values. The primary aim of our study was to find out whether it would be possible to detect platinum NMR signals from adsorbed species and to determine their structures.

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An analysis of available literature data on ^{195}Pt NMR of Pt(IV) complexes in liquid solutions and solid state, which were summarized in several reviews,^{13–16} reveals that this technique has many important advantages and may be an excellent tool for the characterization of adsorbed platinum species: (i) ^{195}Pt NMR measurements are rather easy on modern Fourier transform NMR spectrometers. (ii) The total platinum chemical shift range is very large (about 15 000 ppm); therefore, it is relatively easy to discriminate Pt(IV) complexes of different structures from their ^{195}Pt chemical shift, which is highly sensitive to the ligand environment. (iii) As follows from ^{195}Pt MAS NMR spectroscopy data,^{17,18} solid hexachloroplatinates(IV) (for instance, $(\text{NH}_4)_2\text{PtCl}_6$ and K_2PtCl_6) exhibit only very small chemical shift anisotropy (<5 ppm) due to the high symmetry of the PtCl_6 unit. As a result, ^{195}Pt NMR signals of powder K_2PtCl_6 are readily observable under static conditions, the line width being comparable to that in the MAS NMR spectra (34 and 24 ppm, respectively).¹⁸

Thus, it appears that there is a good chance to observe ^{195}Pt NMR signals from adsorbed Pt(IV) species, if they have a regular or slightly distorted octahedral symmetry. However, to the best of our knowledge, no ^{195}Pt NMR spectroscopy data on the H_2PtCl_6 solution–alumina interface have been reported so far. We were able to find in the literature only one example of the application of ^{195}Pt MAS NMR spectroscopy to the study of γ -alumina impregnated with an H_2PtCl_6 solution and dried at 20 °C and then at 120 °C for 24 h.⁵ The observed NMR signals were assigned to $[\text{PtCl}_6]^{2-}$ octahedra in H_2PtCl_6 crystals, which start to grow at loadings above 1 mmol of H_2PtCl_6 per m^2 of Al_2O_3 . Below this limit, platinum complexes adsorb strongly on the support, and no NMR signals were detected that could be attributed to such adsorbed species. It was concluded⁵ that the variation in the chemical environment of these strongly adsorbed complexes, which arise from the exchange of one or more chloride ions in $[\text{PtCl}_6]^{2-}$ for an oxygen ion or a hydroxyl group of the support, give rise to a large spread in ^{195}Pt chemical shifts and therefore to broad peaks of low intensity, which are difficult to observe.

It should be mentioned here that a number of papers concerning Knight shift and relaxation-time measurements in small Pt metal particles dispersed on oxides (Al_2O_3 , SiO_2 , and TiO_2)^{19–25} and zeolites²⁶ are out of the scope of this work and therefore will not be discussed here.

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Our preliminary report on the applicability of ^{195}Pt NMR spectroscopy for studies of H_2PtCl_6 adsorption on γ - Al_2O_3 and SiO_2 has been published elsewhere.²⁷

Experimental Section

Materials and Procedures. Spherical beads of γ -alumina (cubic) were provided by Procatalyse. The specific surface area was 195 m^2/g , and the total pore volume was 0.6 cm^3/g . Prior to adsorption experiments, alumina beads were crushed in a mortar, and the fraction of the resulting powder with particle size ranging from 180 to 250 μm was separated with use of calibrated sieves.

Two different stock solutions were prepared by diluting with water a 8 wt % aqueous solution of H_2PtCl_6 (Aldrich): $[\text{Pt}] = 1.2 \times 10^{-2}$ M at $\text{pH}_0 = 1.8$ and $[\text{Pt}] = 6.6 \times 10^{-2}$ M at $\text{pH}_0 = 1.0$. The pH values of the solutions were measured by using a Tacussel digital pH meter with a combination glass/reference Radiometer XC200 electrode. No change in pH values was found to occur for the aged stock solutions.

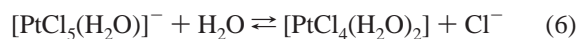
Both stock solutions were used for ^{195}Pt NMR measurements, whereas adsorption experiments were performed with the 1.2×10^{-2} M solution. The $\text{Al}_2\text{O}_3/\text{Pt}$ ratios in the adsorption experiments were 21.4 g/g.

^{195}Pt NMR Measurements. The 85.9-MHz ^{195}Pt NMR spectra were recorded at room temperature with a Bruker MSL-400 instrument equipped with a multinuclear probe for liquid-state NMR. A simple one-pulse sequence was employed; pulse duration was 8 ms, dead time before acquisition was 20 ms, and equilibration time between two pulses was 0.5 s. In MAS NMR experiments with the same pulse sequence, the spinning rate of the sample was 5 kHz. Due to the wide range of ^{195}Pt chemical shifts (δ_{Pt}) and the relatively small line widths, rather large observation windows (62 500 or 125 000 Hz) and a great number of data points (32 K) were required. Line broadening factors of 25 Hz were introduced to improve the signal-to-noise ratio during the Fourier transformation. The ^{195}Pt chemical shifts (δ_{Pt}) were referenced to the $[\text{PtCl}_6]^{2-}$ signal ($\delta_{\text{Pt}} = 0$ ppm) in the starting 0.2 M H_2PtCl_6 solution. In some cases, small deviations from $\delta_{\text{Pt}} = 0$ ppm (up to ~ 2 ppm) were noticed for the $[\text{PtCl}_6]^{2-}$ signal in dilute H_2PtCl_6 solutions, which may arise from a drift of the magnetic field (no lock) during prolonged NMR measurements. However, the differences in chemical shift of Pt species in the spectra of a given solution or solid were always constant within ± 0.2 ppm. Acquisition times varied from 30 min to ~ 12 h (overnight acquisition).

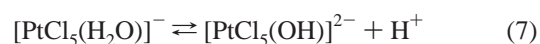
Results and Interpretation

^{195}Pt NMR of H_2PtCl_6 Solutions. Preliminary Consideration and Literature Data. Prior to studying adsorption of H_2PtCl_6 on alumina, it was considered worthwhile to examine aqueous solutions of H_2PtCl_6 at various pH values by ^{195}Pt NMR.

H_2PtCl_6 is a strong acid, and $[\text{PtCl}_6]^{2-}$ anions which result from dissociation of the acid are readily hydrolyzed in an aqueous medium to give rise to a variety of chloroaqua and chlorohydroxo platinum complexes. The hydrolysis of $[\text{PtCl}_6]^{2-}$ in neutral or slightly acidic aqueous solutions at temperatures below 50 °C occurs by the following sequence of reactions:^{2,4}



The chloroaqua platinum complexes behave like weak acids:



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Table 1. Literature Data on the ^{195}Pt Chemical Shift (δ_{Pt}) for $[\text{Pt}^{\text{IV}}\text{Cl}_5\text{X}]$ and $[\text{Pt}^{\text{IV}}\text{Cl}_4\text{X}_2]$ Complexes ($\text{X} = \text{H}_2\text{O}$ or OH^-) in Aqueous Solutions

complex	δ_{Pt} , ppm	preparation procedure and pH of solution	ref
$[\text{PtCl}_6]^{2-}$	0 (reference)		
$[\text{PtCl}_5(\text{H}_2\text{O})]^-$	475	<i>a</i>	28
$[\text{PtCl}_5(\text{aq})]^b$	504	<i>c</i>	29
$[\text{PtCl}_5(\text{OH})]^{2-}$	666	<i>d</i>	29
$[\text{PtCl}_4(\text{H}_2\text{O})_2]^e$	1029	<i>f</i>	28
<i>cis</i> - $[\text{PtCl}_4(\text{aq})_2]^b$	1005	<i>c</i>	29
<i>trans</i> - $[\text{PtCl}_4(\text{aq})_2]^b$	1126	<i>c</i>	29
<i>cis</i> - $[\text{PtCl}_4(\text{OH})_2]^{2-}$	1281	<i>d</i>	29
<i>trans</i> - $[\text{PtCl}_4(\text{OH})_2]^{2-}$	1263	<i>d</i>	29

^a Oxidation of $[\text{Pt}^{\text{II}}\text{Cl}_4]^{2-}$ in a 0.1 M aqueous solution with excess chlorine; pH is not specified. ^b (aq) is used in ref 29 to indicate that OH ligands have acquired some unspecified degree of additional protonation. ^c Hydrolysis of $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$ in an acid aqueous solution at pH 1–3. ^d Boiling of $\text{Ag}_2[\text{Pt}^{\text{IV}}\text{Cl}_6]$ in water and adjusting pH to ca. 10. ^e No indication on *cis* or *trans* configuration. ^f Addition of excess chlorine to a 0.15 M aqueous solution of $[\text{Pt}^{\text{II}}(\text{H}_2\text{O})_4]^{2+}$ and aging the solution for a period of several months; pH is not specified.



The resulting chloroaqua and chlorohydroxo platinum complexes can be distinguished by their ^{195}Pt chemical shifts (δ_{Pt}) in NMR spectra. However, to the best of our knowledge, no systematic ^{195}Pt NMR study has been undertaken so far to elucidate the speciation of $[\text{PtCl}_6]^{2-}$ anions in H_2PtCl_6 aqueous solutions as a function of pH and/or of the time of hydrolysis. Available literature data on ^{195}Pt NMR of $\text{Pt}^{\text{IV}}\text{Cl}_{6-n}(\text{H}_2\text{O})_n$ and $\text{Pt}^{\text{IV}}\text{Cl}_{6-n}(\text{OH})_n$ complexes ($n = 1$ or 2) are scarce and rather contradictory (Table 1). No ^{195}Pt NMR spectrum has been reported for $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$.

Nevertheless, the data of Table 1 clearly show that the ^{195}Pt chemical shift is strongly dependent on the chemical composition of the first coordination sphere of the Pt ion. The substitution of one Cl^- ligand in $[\text{PtCl}_6]^{2-}$ with H_2O or OH^- causes very large chemical shifts (ca. 500 ppm for H_2O and ca. 660 ppm for OH^-) and the substitution of the second Cl^- with H_2O or OH^- gives rise to an increase in δ_{Pt} to 1000–1280 ppm. This makes it relatively easy to identify PtCl_6 , PtCl_5X , and PtCl_4X_2 ($\text{X} = \text{H}_2\text{O}$ or OH^-) in aqueous H_2PtCl_6 solutions by the ^{195}Pt chemical shift. The data of Table 1 show that the substitution of Cl^- with OH^- in the platinum coordination sphere results in a greater δ_{Pt} than the substitution with H_2O . It is also evident that δ_{Pt} of partially hydrolyzed Pt species is pH sensitive and decreases on acidification. Although not clearly stated in the references of Table 1, this effect might indicate fast proton exchange between aqua and hydroxo platinum complexes.

The literature data on δ_{Pt} for $[\text{PtCl}_4(\text{OH})_2]^{2-}$ and $[\text{PtCl}_4(\text{aq})_2]$ complexes in *cis* or *trans* configurations are rather confusing. On the one hand, $\delta_{\text{Pt}}(\text{cis}) > \delta_{\text{Pt}}(\text{trans})$ was reported²⁹ for $[\text{PtCl}_4(\text{OH})_2]^{2-}$ at pH = 10–12 with a relatively small difference in δ_{Pt} (18 ppm). On the other hand, the same authors found $\delta_{\text{Pt}}(\text{cis}) < \delta_{\text{Pt}}(\text{trans})$ for $[\text{PtCl}_4(\text{aq})_2]$ at pH = 1–3 with a greater difference in δ_{Pt} (121 ppm). In another study, a single NMR line at $\delta_{\text{Pt}} = 1029$ ppm was reported²⁸ for $[\text{PtCl}_4(\text{H}_2\text{O})_2]$ produced by a prolonged aging of aqueous solutions of $[\text{PtCl}_6]^{2-}$.

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$(\text{H}_2\text{O})_5]^{3+}$ on the assumption that the signals from *cis* and *trans* forms are closely spaced.

^{195}Pt NMR of Freshly Prepared and Aged H_2PtCl_6 Solutions. Let us now consider ^{195}Pt NMR spectra for two series of H_2PtCl_6 aqueous solutions at different pH values. The pH was adjusted to a desired value by adding 1 or 0.1 M NaOH solutions to the stock H_2PtCl_6 solutions $[\text{Pt}] = 1.2 \times 10^{-2}$ M at $\text{pH}_0 = 1.8$ and $[\text{Pt}] = 6.6 \times 10^{-2}$ M at $\text{pH}_0 = 1.0$. NMR acquisitions were started within 5–10 min after the preparation.

The representative NMR spectra of the solutions are shown in Figures 1 and 2, and peak positions are listed in Table 2. Platinum resonances are observed in three separate ranges of chemical shift (δ_{Pt}): (i) $\delta_{\text{Pt}} = 0$ ppm ($[\text{PtCl}_6]^{2-}$ reference), (ii) $\delta_{\text{Pt}} = 504$ –661 ppm, and (iii) $\delta_{\text{Pt}} = 1005$ –1271 ppm. While further discriminations will have to be made later, it is obvious from the data of Table 1 that the species resonating in range (ii) correspond to pentachloroplatinates $[\text{PtCl}_5\text{X}]$, and those in range (iii) are tetrachloroplatinates $[\text{PtCl}_4\text{X}_2]$ ($\text{X} = \text{H}_2\text{O}$ or OH^-). Note that the latter species are minor in the solutions studied, i.e., the hydrolysis of $[\text{PtCl}_6]^{2-}$ occurs predominantly by reaction 5.

An examination of the ^{195}Pt NMR spectra in Figures 1 and 2 and the data of Table 2 reveals that the chemical shift of some Pt species is pH dependent. As the pH of H_2PtCl_6 solutions increases, the NMR signals at 504 and 1005 ppm continuously move to higher δ_{Pt} values (to the final values of 661 and 1271 ppm, respectively), whereas the NMR signal of $[\text{PtCl}_6]^{2-}$ ($\delta_{\text{Pt}} = 0$ ppm) remains at a constant value of δ_{Pt} . Possible reasons for such behavior will be discussed below.

It was found that strongly acidic solutions (at $\text{pH} \leq 2$) are stable and exhibit no change in pH at room temperature, whereas the pH of less acidic solutions decreases considerably with time (Table 2). Correspondingly, significant changes in ^{195}Pt NMR spectra were observed for the aged H_2PtCl_6 solutions.

Figures 1f,g and 2 enable one to compare the NMR spectra of some “fresh” and “aged” H_2PtCl_6 solutions. No marked change was found to occur in the stock solutions at initial $\text{pH}_0 = 1.8$ and 1.35, whereas the aging of solutions with higher initial pH results in shifting the penta- and tetrachloroplatinate resonances to lower δ_{Pt} values. Note that the spectra of the aged 1.2×10^{-2} M solutions are rather similar, since their pH’s are close (Figure 2).

For strongly acidic solutions, in which deprotonation reactions 7–9 are fully suppressed by high concentrations of protons, one may expect to observe three types of Pt species, namely $[\text{PtCl}_6]^{2-}$, $[\text{PtCl}_5(\text{H}_2\text{O})]^-$, and $[\text{PtCl}_4(\text{H}_2\text{O})_2]$ (possibly, *cis* and *trans*). This situation corresponds to the spectrum of a 6.6×10^{-2} M solution at pH 1.0–1.35 (Figure 1a) in which three resonances at $\delta_{\text{Pt}} = 0$, 504, and 1005 ppm are detected. These signals can therefore be assigned to $[\text{PtCl}_6]^{2-}$, $[\text{PtCl}_5(\text{H}_2\text{O})]^-$, and $[\text{PtCl}_4(\text{H}_2\text{O})_2]$, respectively (Table 3). Since only one peak is observed for $[\text{PtCl}_4(\text{H}_2\text{O})_2]$, we may conclude that either the difference in δ_{Pt} for *cis* and *trans* isomers is so small that the two closely spaced peaks are not resolved, or the fraction of one of the isomers is so small that the corresponding peak cannot be detected.

On the other hand, for the most basic solutions, in which deprotonation/protonation equilibria 7–9 are profoundly shifted to the right, one may expect to find NMR signals of $[\text{PtCl}_6]^{2-}$, $[\text{PtCl}_5(\text{OH})]^{2-}$, and $[\text{PtCl}_4(\text{OH})_2]^{2-}$ complexes. This situation corresponds to the spectra of 1.2×10^{-2} M solution at pH = 11.4 (Figure 2c). Hence, the 661 and 1271 ppm lines can be assigned to $[\text{PtCl}_5(\text{OH})]^{2-}$, and $[\text{PtCl}_4(\text{OH})_2]^{2-}$, respectively (Table 3). Again, only one peak is observed for *cis*- and *trans*-

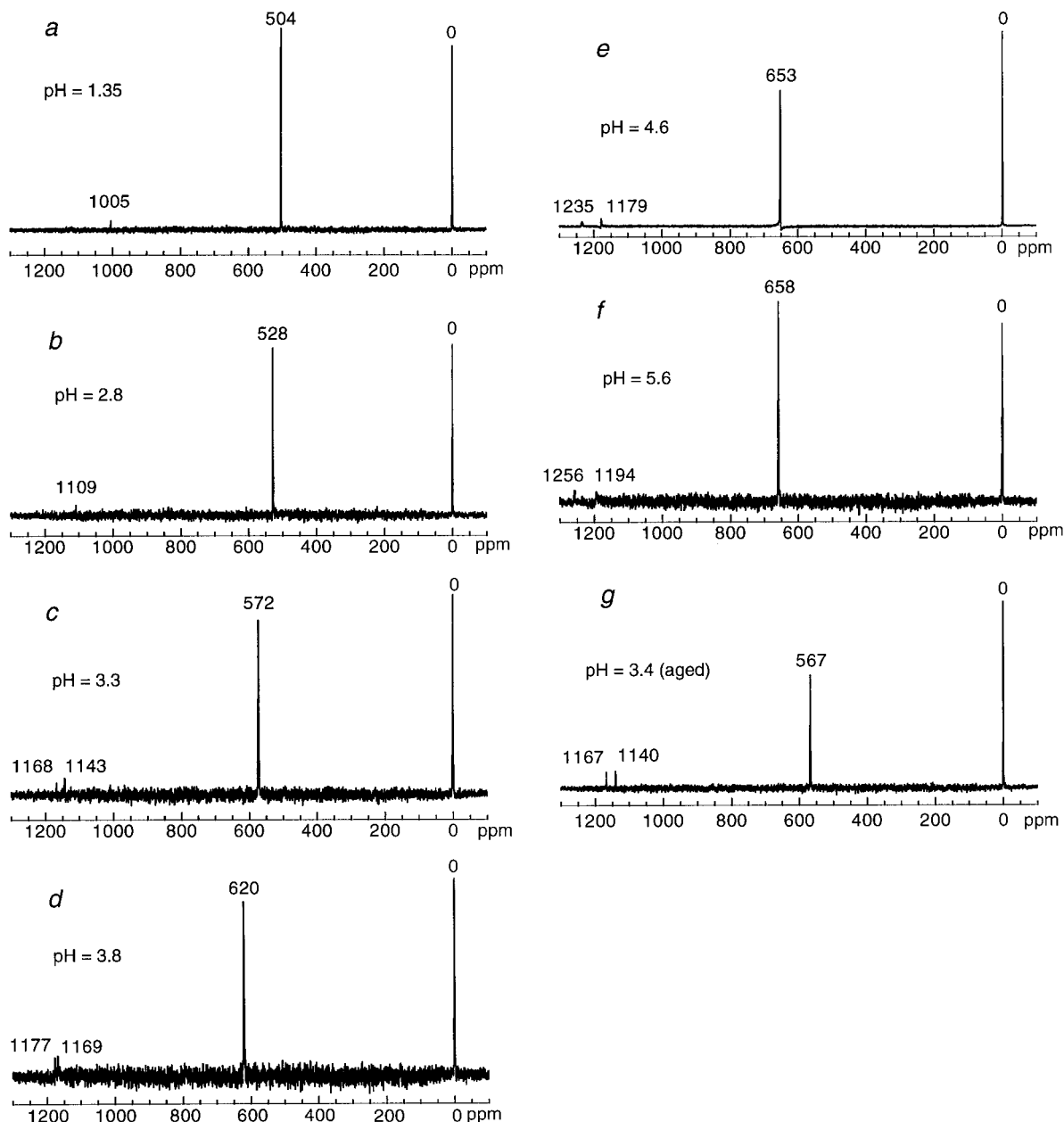


Figure 1. ^{195}Pt NMR of fresh (a–f) and aged (g) 6.6×10^{-2} M H_2PtCl_6 aqueous solutions at the pH indicated.

$[\text{PtCl}_4(\text{OH})_2]^{2-}$, which is indicative of either a small difference in δ_{Pt} for both isomers or the predominance of one of these isomers.

In the intermediate pH range (3.3–5.6), two resonances are observed in the tetrachloroplatinate range (peaks A and B, Table 2). A conceivable explanation of this phenomenon will be presented below.

The continuous shift of the 504 ppm line to higher δ_{Pt} values at increasing pH suggests fast proton exchange between $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ and $[\text{PtCl}_5(\text{OH})]^{2-}$ (reaction 7). If protonation–deprotonation is fast on the NMR time scale, one would expect to observe only one signal instead of two, with a chemical shift that would be the concentration-weighted average of the values for $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ and $[\text{PtCl}_5(\text{OH})]^{2-}$. The position of the averaged signal (δ_{Pt}) is then determined by the following

equation:³⁰

$$\delta_{\text{Pt}} = (\delta_{\text{Pt(A)}}[\text{H}^+] + \delta_{\text{Pt(B)}}K_a)/([\text{H}^+] + K_a) \quad (\text{I})$$

where K_a is the acid dissociation constant for $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ and $\delta_{\text{Pt(A)}}$ and $\delta_{\text{Pt(B)}}$ are the chemical shifts of $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ and $[\text{PtCl}_5(\text{OH})]^{2-}$, respectively.

Figure 3a demonstrates the plot of δ_{Pt} for the pentachloroplatinate complexes vs pH of the solutions. Note that the points for the “fresh” and “aged” solutions fall well on the same curve.

The value of $\text{p}K_a$ for $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ that gives the best (least-squares) fit of eq I to the experimental data of Figure 3a was calculated as $\text{p}K_a = 3.48 \pm 0.04$ with the correlation coefficient $R^2 = 0.99$. This value is comparable to $\text{p}K_a = 3.8$ found earlier by Davidson and Jameson³¹ for K_2PtCl_6 solutions using fast microtitration with NaOH.

Figure 3b shows the plots of δ_{Pt} for the tetrachloroplatinate complexes as a function of pH. Similarly to the pentachloroplatinate complexes, the continuous shift of the 1005 ppm line

(30) Barton, S. J.; Barnham, K. J.; Habtemariam, A.; Sue, R. E.; Sadler, P. J. *Inorg. Chim. Acta* **1998**, *273*, 8–13.

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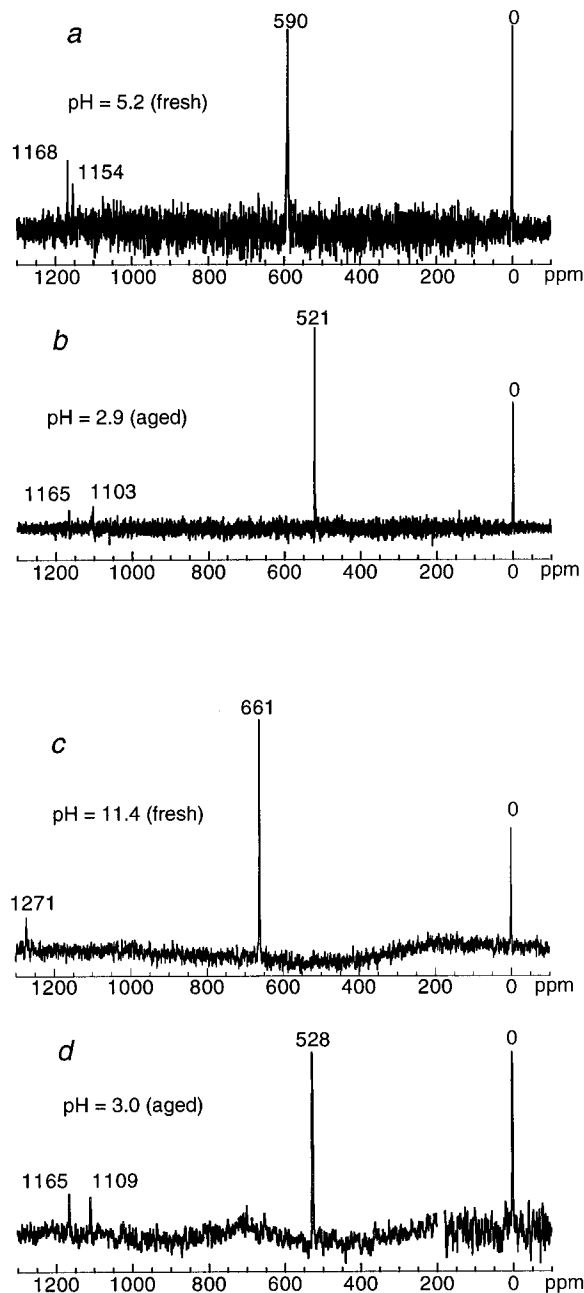


Figure 2. ^{195}Pt NMR of fresh (a, c) and aged (b, d) 1.2×10^{-2} M H_2PtCl_6 aqueous solutions at the pH indicated.

to higher δ_{Pt} values at increasing pH of the solutions can be explained by assuming fast proton exchange between $[\text{PtCl}_4(\text{H}_2\text{O})_2]$, $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$, and $[\text{PtCl}_4(\text{OH})_2]^{2-}$ (reactions 8 and 9). In this case, the position of the averaged single peak is given by the following equation:³⁰

$$\delta_{\text{Pt}} = (\delta_{\text{Pt}(\text{AB})} + \delta_{\text{Pt}(\text{AA})}[\text{H}^+]/K_{\text{a1}} + \delta_{\text{Pt}(\text{BB})}K_{\text{a2}}/[\text{H}^+]) / (1 + [\text{H}^+]/K_{\text{a1}} + K_{\text{a2}}/[\text{H}^+]) \quad (\text{II})$$

where K_{a1} and K_{a2} stand for the acid dissociation constants for $[\text{PtCl}_4(\text{H}_2\text{O})_2]$ and $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$, respectively, and $\delta_{\text{Pt}(\text{AA})}$, $\delta_{\text{Pt}(\text{AB})}$, and $\delta_{\text{Pt}(\text{BB})}$ are the chemical shifts of $[\text{PtCl}_4(\text{H}_2\text{O})_2]$, $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$, and $[\text{PtCl}_4(\text{OH})_2]^{2-}$, respectively.

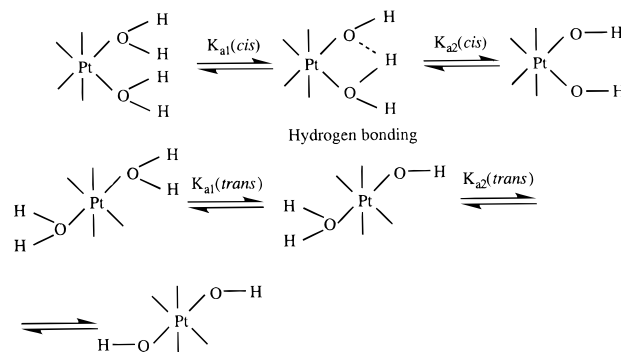
The similar course of curves 1 and 2 in Figure 3b at lower ($\text{pH} < 3$) and higher ($\text{pH} > 7$) pH values and the presence of two lines at intermediate pH's can be rationalized by assuming that (i) the peak positions of the cis and trans forms are too

Table 2. Peak Positions in the ^{195}Pt NMR Spectra of H_2PtCl_6 Solutions

pH ^a	peak position (δ_{Pt}), ppm ^b		
	PtCl ₅ X range	PtCl ₄ X ₂ range	
		A ^c	B ^c
6.6×10^{-2} M H_2PtCl_6 solution			
1.0 (f)	504	1005	
1.35 (f)	504	1005	
2.8 (f)	528	1109	
3.3 (f)	572	1168	1143
3.8 (f)	620	1177	1169
4.6 (f)	653	1235	1179
5.6 (f)	658	1256	1194
3.4 (a)	567	1167	1140
1.2×10^{-2} M H_2PtCl_6 solution			
1.8 (f)	504	1017	
1.8 (a)	504	1017	
3.0 (f)	519	1166	1099
2.7 (a)	514	1164	1087
3.9 (f)	544	1167	1128
2.8 (a)	524	1166	1107
5.2 (f)	590	1168	1154
2.9 (a)	521	1165	1103
6.2 (f)	658	1258	
2.9 (a)	523	1166	1106
7.0 (f)	661	1268	
2.8 (a)	524	1166	1107
10.9 (f)	662	1274	1256
3.0 (a)	520	1166	1100
11.4 (f)	661	1271	
3.0 (a) ^d	528	1165	1109

^a (f) is pH of the "fresh" solutions; (a) is pH of the "aged" solutions after 1–2 days. ^b Peak positions are indicated relative to the $[\text{PtCl}_6]^{2-}$ signal at $\delta_{\text{Pt}} = 0$ ppm. ^c Peaks A and B correspond to points on curves 1 and 2 of Figure 3, respectively. ^d After 100 days.

close to be resolved and (ii) the acid dissociation constants and especially K_{a2} differ substantially for *cis*- and *trans*- $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$. This difference may arise due to hydrogen bonding of the proton of the water ligand with adjacent hydroxyl in the *cis* isomer, which hinders deprotonation of the second water ligand as illustrated by the following scheme.



The best fit of eq II to the experimental data of Figure 3b agrees well with the above assumption. It gives for curves 1 and 2 the following values: $\text{p}K_{\text{a1}}(\text{trans}) = 2.64 \pm 0.13$, $\text{p}K_{\text{a2}}(\text{trans}) = 4.49 \pm 0.18$, and $\delta_{\text{Pt}(\text{AB})} = 1181 \pm 15$ ppm (*trans*- $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$) with $R^2 = 0.99$; $\text{p}K_{\text{a1}}(\text{cis}) = 2.78 \pm 0.09$, $\text{p}K_{\text{a2}}(\text{cis}) = 6.25 \pm 0.28$, and $\delta_{\text{Pt}(\text{AB})} = 1177 \pm 8$ ppm (*cis*- $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$) with $R^2 = 0.99$.

The K_{a1} values for *trans*- and *cis*- $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$ are very close and lie within the uncertainties in the fitting coefficients. In contrast, the K_{a2} value for *trans*- $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$ is found

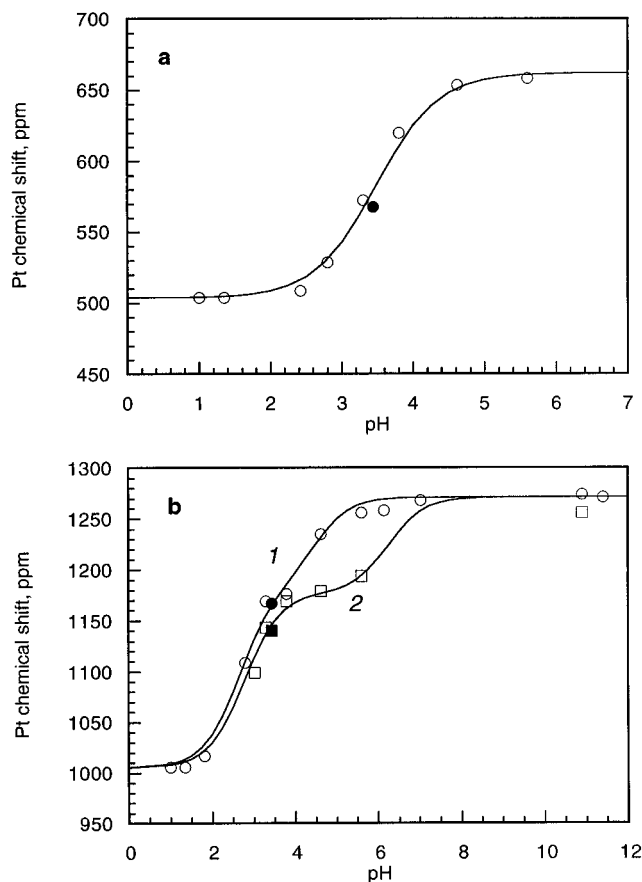


Figure 3. Plots of Pt chemical shifts vs pH of H_2PtCl_6 solutions: (a) pentachloroplatinate complexes; (b) tetrachloroplatinate complexes. Points on curves 1 (circles) and 2 (squares) correspond to the positions of peaks A and B, respectively (Table 2). Open symbols, fresh solutions; solid symbols, aged solutions. The curves are the best fits giving the $\text{p}K_a$ values described in the text.

Table 3. Proposed Assignment for ^{195}Pt NMR Signals Observed in H_2PtCl_6 Aqueous Solutions and Acid Dissociation Constants

species assignment	δ_{Pt} , ppm	$\text{p}K_a$
$[\text{PtCl}_6]^{2-}$	0 (reference)	
$[\text{PtCl}_5(\text{H}_2\text{O})]^-$	504	3.48 ± 0.04
$[\text{PtCl}_5(\text{OH})]^{2-}$	662	
$(\text{cis}, \text{trans}) [\text{PtCl}_4(\text{H}_2\text{O})_2]$	1005	$(\text{cis}) 2.78 \pm 0.09$ $(\text{trans}) 2.64 \pm 0.13$
$(\text{cis}, \text{trans}) [\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$	1176 ± 10^a	$(\text{cis}) 6.25 \pm 0.28$ $(\text{trans}) 4.49 \pm 0.18$
$(\text{cis}, \text{trans}) [\text{PtCl}_4(\text{OH})_2]^{2-}$	1271	

^a Not observed in the NMR spectra. An estimate made from the best fit of the δ_{Pt} vs pH dependence of Figure 3b.

to be approximately 2 orders of magnitude higher than the K_{a2} - (cis) value, indicating much more difficult deprotonation of the latter isomer. We were unable to find reliable literature data for $\text{p}K_{a1}$ and $\text{p}K_{a2}$. The rough estimates for the acid dissociation constants reported in ref 32 ($\text{p}K_{a1} \sim 4.2$ and $\text{p}K_{a2} \sim 6.2$) and in ref 33 ($\text{p}K_{a1} = 1.9$ and $\text{p}K_{a2} = 5.5$) for $\text{trans}-[\text{PtCl}_4(\text{H}_2\text{O})_2]$ are rather far away from the values found in this work.

As seen from Tables 1 and 3, the effects of ligand substitution on ^{195}Pt chemical shifts are roughly additive. The δ_{Pt} values calculated for $\text{trans}-$ and $\text{cis}-[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$ are in reasonable agreement with what one may expect to observe for this complex assuming that the substitution of one Cl ligand in

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(33) Cox, L. E.; Peters, D. G. *Inorg. Chem.* **1970**, *9*, 1927–1930.

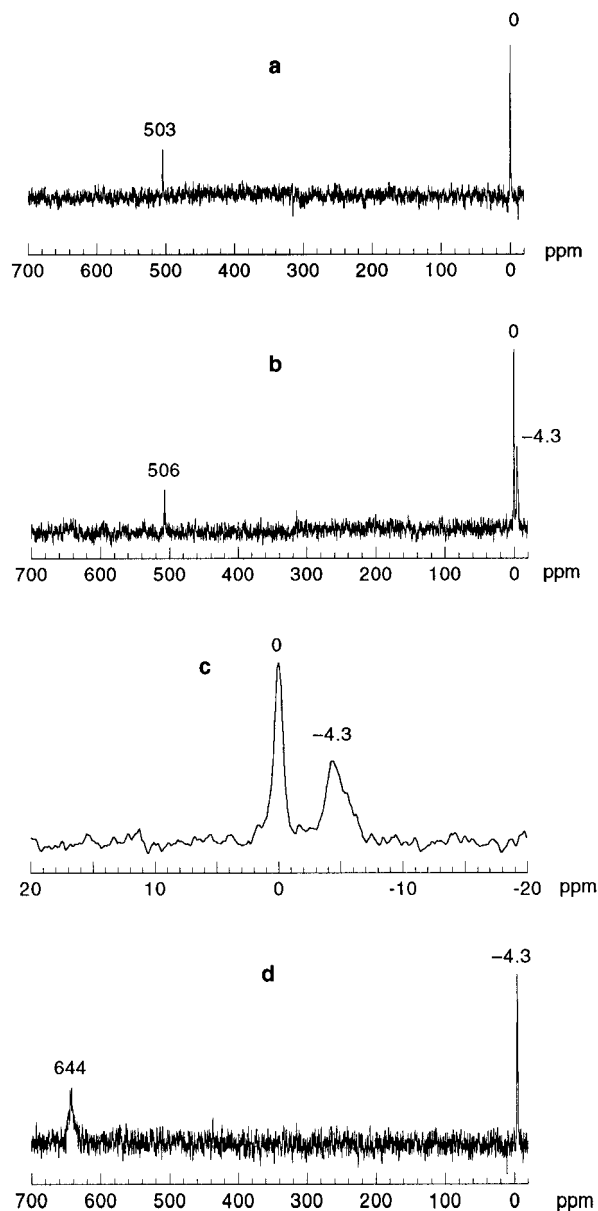


Figure 4. ^{195}Pt NMR spectra of (a) a 1.2×10^{-2} M H_2PtCl_6 solution at pH 1.2, (b) a $\text{H}_2\text{PtCl}_6\text{-Al}_2\text{O}_3$ mixture obtained by adding 0.25 g of Al_2O_3 to 5 mL of the solution in a, (c) a detailed view of the $[\text{PtCl}_6]^{2-}$ signals of spectrum b; and (d) rinsed Al_2O_3 powder positioned in the center of the NMR probe.

$[\text{PtCl}_6]^{2-}$ by H_2O would result in a 504 ppm shift, and the substitution of another Cl ligand by OH would add a 662 ppm shift (1166 ppm) (Table 3).

It should be noted that K_{a1} for $[\text{PtCl}_4(\text{H}_2\text{O})_2]$ is considerably higher than K_a for $[\text{PtCl}_5(\text{H}_2\text{O})]^-$, that is, the diaqua complex is a much stronger acid than the monoqua form, probably because the former bears no charge, while the latter is negatively charged.

The slow decrease in pH observed after basification of $\text{H}_2\text{-PtCl}_6$ solutions (the effect of solution “aging”) indicates that the hydrolysis of $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ (reactions 5 and 6) occurs relatively slowly at room temperature. This is in line with the conclusions drawn in refs 31 and 32 from pH measurements and titration curves for aqueous solutions of $\text{K}_2\text{-[PtCl}_6]$ in the temperature range 25–55 °C.

^{195}Pt NMR of $\text{H}_2\text{PtCl}_6\text{-Al}_2\text{O}_3$ Mixtures. Figure 4a shows the ^{195}Pt NMR spectrum of a H_2PtCl_6 solution at pH = 1.2, and Figure 4b is the spectrum of a mixture obtained by

0.25 g of Al_2O_3 to 5 mL of that solution. A remarkable feature of the spectrum in Figure 4b is the appearance of a second $[\text{PtCl}_6]^{2-}$ signal with a small negative chemical shift ($\delta_{\text{Pt}} = -4.3$ ppm). A detailed view of these two $[\text{PtCl}_6]^{2-}$ lines is presented in Figure 4c. Note that the -4.3 ppm line is markedly broader than the $[\text{PtCl}_6]^{2-}$ signal in the solution (line widths at half-height (lwhh) are 2.13 and 0.98 ppm, respectively). The $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ lines at $\delta_{\text{Pt}} = 503$ or 506 ppm are also seen in Figures 4a and 4b.

Most likely, the -4.3 ppm signal arises from adsorbed $[\text{PtCl}_6]^{2-}$. The small negative shift and broadening of this signal could result from a weak interaction of $[\text{PtCl}_6]^{2-}$ anions with the alumina surface that slightly perturbs the ligand sphere of the central Pt ion. Such perturbation may arise from polarization effects due to the strong electric field in the vicinity of a charged surface, although hydrogen bonding cannot be ruled out. The following experiment was conducted to prove the assignment.

The alumina powder stored overnight under the H_2PtCl_6 solution was decanted and then rinsed twice with distilled water. Following this procedure, the rinsed powder in the NMR tube was positioned approximately in the center of the receiver-coil area of the NMR probe to provide better conditions for detecting signals from adsorbed platinum species (Figure 4d). The $\delta_{\text{Pt}} = 0$ ppm line disappeared, whereas the -4.3 ppm signal was preserved thus confirming the assignment of the latter signal to adsorbed $[\text{PtCl}_6]^{2-}$. Conceivable reasons for broadening of this signal will be discussed below.

In addition to the -4.3 ppm peak, a rather broad line (line width at half-height is 5.7 ppm) at $\delta_{\text{Pt}} = 644$ ppm appears in Figure 4d that can be attributed to adsorbed $[\text{PtCl}_5(\text{OH})]^{2-}$ (Table 3).

In another experiment, we succeeded in simultaneously observing NMR signals arising from the adsorbed Pt species and those in the solution. When 0.25 g of alumina was added to 5 mL of an H_2PtCl_6 solution at pH = 1.8, whose spectrum is presented in Figure 5a, the spectrum shown in Figure 5b was obtained. The signal-to-noise ratio in the latter spectrum is rather poor because of unfavorable conditions for detecting ^{195}Pt NMR signals from both the solution and the powder: the solution is depleted in platinum anions due to adsorption on alumina, whereas the alumina powder with adsorbed platinum species is at the bottom of the NMR tube and thus away from the most sensitive central area of the NMR probe. Nevertheless, four lines are clearly seen in Figures 5b and 5c: two are associated with the solution at $\delta_{\text{Pt}} = 1.2$ ppm ($[\text{PtCl}_6]^{2-}$) and at $\delta_{\text{Pt}} = 512$ ppm ($[\text{PtCl}_5(\text{H}_2\text{O})]^- \leftrightarrow [\text{PtCl}_5(\text{OH})]^{2-} + \text{H}^+$) and two with the solid at $\delta_{\text{Pt}} = -2.5$ ppm (adsorbed $[\text{PtCl}_6]^{2-}$) and at $\delta_{\text{Pt}} = 650$ ppm (adsorbed $[\text{PtCl}_5(\text{OH})]^{2-}$). When the alumina powder of the same mixture was positioned in the center of the NMR probe, the spectrum shown in Figure 5d was obtained. It consists of only two lines corresponding to the adsorbed platinum complexes as indicated above. Figure 5e is the spectrum of the rinsed alumina powder positioned in the center of the probe. No marked change in the chemical shift of adsorbed platinum species occurred, but the $[\text{PtCl}_5(\text{OH})]^{2-}/[\text{PtCl}_6]^{2-}$ ratio was considerably higher than in the suspension.

Similar spectra were observed when alumina was added to an H_2PtCl_6 solution at a higher initial pH, 3.1 (Figure 6a). Two lines corresponding to adsorbed $[\text{PtCl}_6]^{2-}$ at 0.8 ppm and to $[\text{PtCl}_5(\text{OH})]^{2-}$ at 658 ppm appear in the spectrum of the solid positioned in the center of the probe (not shown). These lines are also present in the spectrum of the rinsed powder accumulated overnight shown in Figure 6b. Again, the $[\text{PtCl}_5(\text{OH})]^{2-}/[\text{PtCl}_6]^{2-}$ ratio markedly increased after washing the

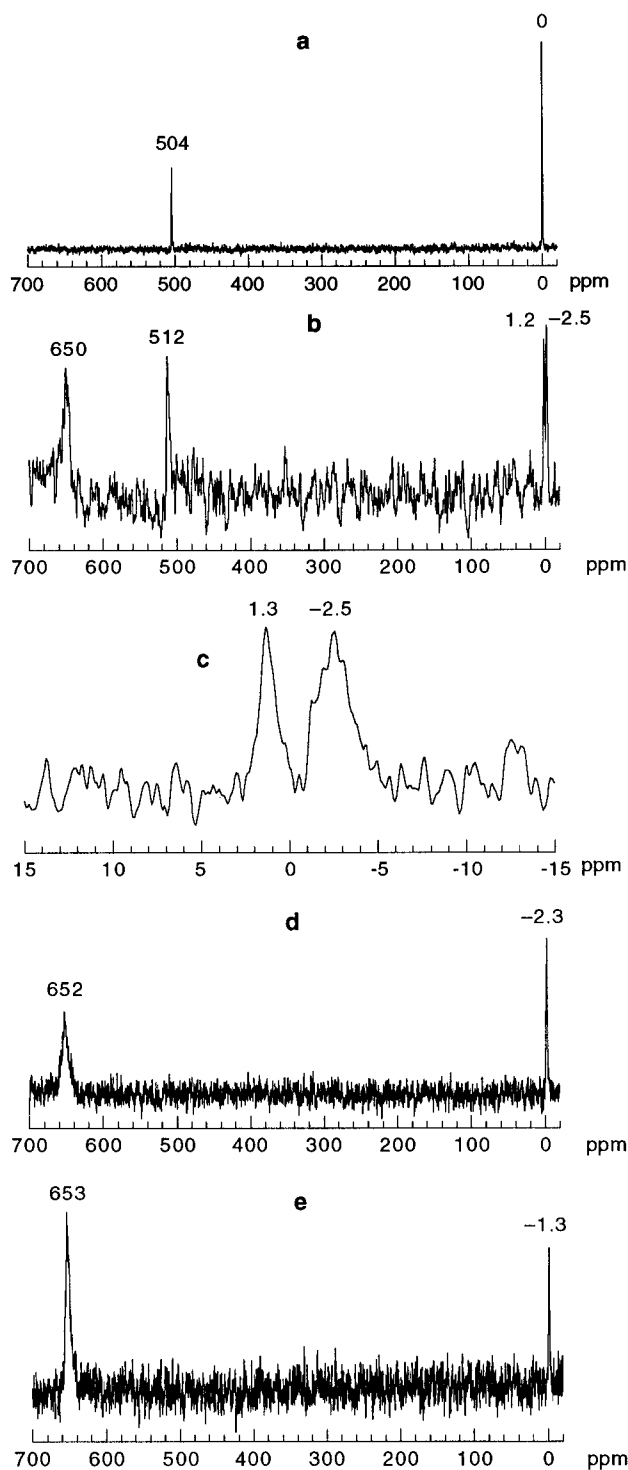


Figure 5. ^{195}Pt NMR of (a) a 1.2×10^{-2} H_2PtCl_6 solution at pH 1.8, (b) a H_2PtCl_6 - Al_2O_3 mixture obtained by adding 0.25 g of Al_2O_3 to 5 mL of the solution in a; (c) a detailed view of the $[\text{PtCl}_6]^{2-}$ signals of spectrum b; (d) Al_2O_3 powder of the mixture in b positioned in the center of the NMR probe; and (e) rinsed Al_2O_3 powder positioned in the center of the NMR probe.

powder with water. Hence, we can conclude that washing favors aquation of $[\text{PtCl}_6]^{2-}$ due to the shift of equilibrium 5 to the right.

Contrary to this, the treatment of the Pt/alumina samples with HCl after the establishment of the initial interaction results in a considerable decrease in the $[\text{PtCl}_5(\text{OH})]^{2-}/[\text{PtCl}_6]^{2-}$ ratio. This effect is illustrated by Figure 7. Curve 1 in Figure 7a is the spectrum of a wet Pt/alumina powder, which was recorded after

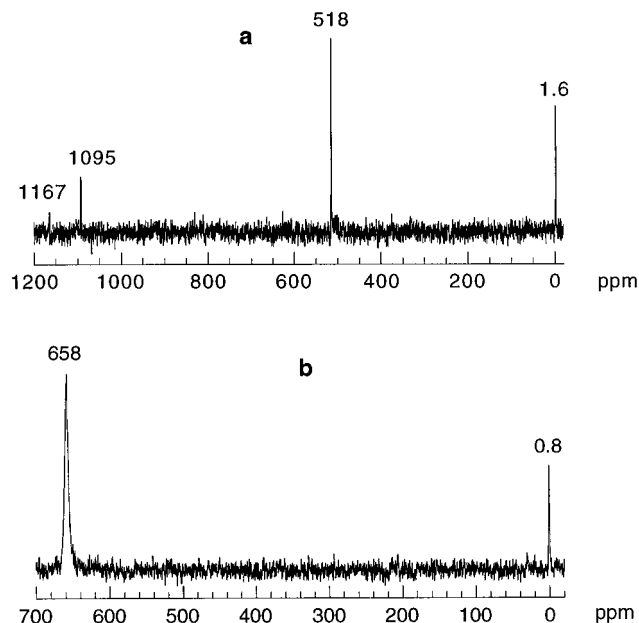


Figure 6. ^{195}Pt NMR of (a) an aged 1.2×10^{-2} H_2PtCl_6 solution at pH 2.3 and (b) a $\text{H}_2\text{PtCl}_6\text{-Al}_2\text{O}_3$ mixture obtained by adding 0.25 g of Al_2O_3 to 5 mL of the solution in a, with the alumina powder rinsed with water and positioned in the center of the NMR probe.

adding 1 g of Al_2O_3 to 10 mL of an H_2PtCl_6 solution at pH = 1.6, stirring the mixture for 3 h, and decanting the excess solution. Curve 2 in Figure 7a is the spectrum of the same solid after adding 2 mL of 0.25 M HCl. The $[\text{PtCl}_5(\text{OH})]^{2-}/[\text{PtCl}_6]^{2-}$ ratio drastically decreased in the latter spectrum because of the shift of equilibria 5–7 to the left due to an increase of the H^+ and Cl^- concentrations. The acid solution in contact with the sample became intensely yellow colored, indicating partial platinum desorption from the surface. This agrees with the data of Mang et al.,³ who found that the amount of platinum adsorbed from acidic H_2PtCl_6 solutions decreased with decreasing pH in the range of pH < 4 due to competitive adsorption of Cl^- on the protonated OH groups. In addition, a second signal at $\delta_{\text{Pt}} = -1.9$ ppm appears in the $[\text{PtCl}_6]^{2-}$ region for the acidified solid (Figure 7b, curve 2), which can tentatively be assigned to $[\text{HPTCl}_6]^-$ adsorbed on the protonated hydroxyls.

Table 4 summarizes NMR data for $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{OH})]^{2-}$ adsorbed on alumina.

No NMR signals were detected in the higher δ_{Pt} region where adsorbed tetrachloroplatinates would be expected to lie. In view of the relatively poor signal-to-noise ratio in the spectra of $\text{H}_2\text{-PtCl}_6\text{-Al}_2\text{O}_3$ mixtures and large line widths of adsorbed species, their presence as minority species cannot be ruled out.

As follows from Table 4, the $[\text{PtCl}_5(\text{OH})]^{2-}/[\text{PtCl}_6]^{2-}$ ratio rises with increasing initial pH, and from the least acidic solution, platinum is adsorbed on the alumina surface predominantly as $[\text{PtCl}_5(\text{OH})]^{2-}$ (Sample 4). Thus, the composition of adsorbed platinum complexes can efficiently be controlled by adjusting the pH values of H_2PtCl_6 solutions and/or by adding HCl after the adsorption is completed.

So far we have discussed the NMR spectra of wet powders. However, the question arises as to whether it would be possible to detect platinum NMR signals from dried powders. To check this possibility, the following experiments were carried out. Approximately 1 g of Al_2O_3 with adsorbed platinum species (Table 4, Sample 2) was dried in a vacuum desiccator at room temperature overnight, i.e., under the conditions that provide a means for the removal of water and allow one to avoid possible decomposition of the adsorbed platinum species. No attempt

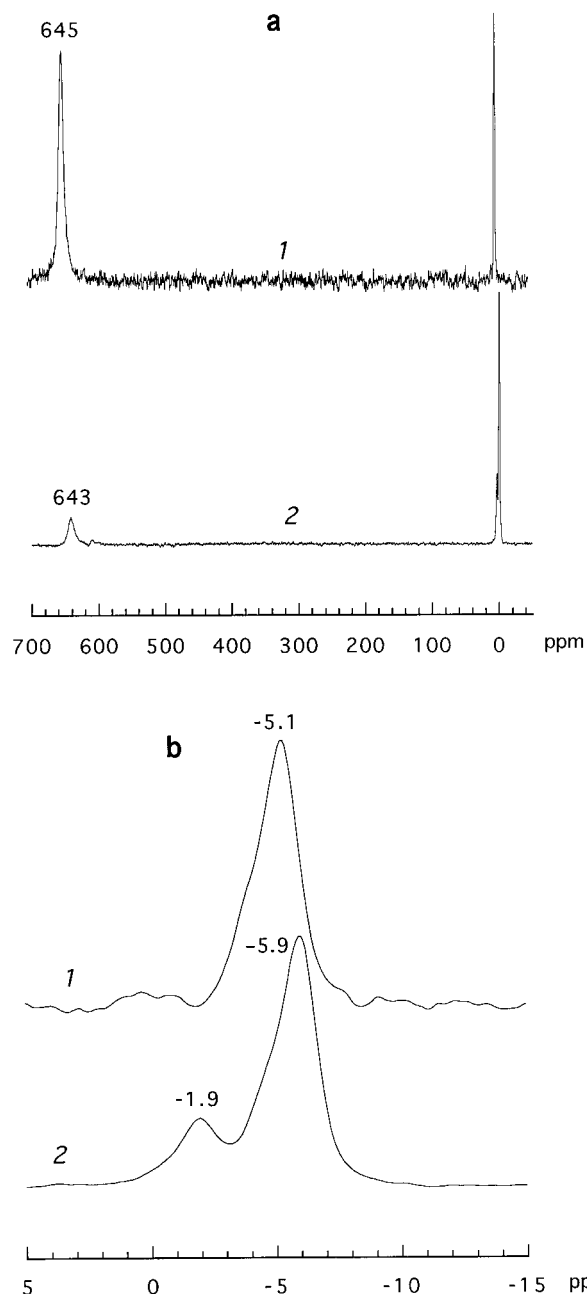


Figure 7. ^{195}Pt NMR of (1) a $\text{H}_2\text{PtCl}_6\text{-Al}_2\text{O}_3$ mixture obtained by adding 1 g of Al_2O_3 to 20 mL of a 1.2×10^{-2} M H_2PtCl_6 solution at pH 1.6 and (2) after adding 2 mL of 0.25 M HCl to the mixture in (1): (a) general view; (b) $[\text{PtCl}_6]^{2-}$ region.

was made to control the amount of remaining water. Following this treatment, no NMR signal could be detected after 10 000 scans. The dried solid was then brought into contact with 2 mL of distilled water. The mixture was homogenized by shaking the sample tube, and the NMR spectrum was then recorded. A spectrum quite similar to that of the original powder was obtained (Figure 8). This indicates that the composition of the adsorbed platinum species does not change appreciably upon drying at room temperature and that the effect of water removal on the NMR spectra is reversible.

On the contrary, after drying the $\text{Pt/Al}_2\text{O}_3$ powder (Sample 2) at 90 °C for 1.5 h, no NMR signal could be detected for the dry solid after more than 10 000 accumulations, and much weaker signals than those in the original solid were observed for the rewetted powder. Thus, water removal at a higher

Table 4. ^{195}Pt NMR Data for Adsorbed Platinum Complexes Obtained by Adsorption on Alumina from H_2PtCl_6 Solutions

sample	pH of initial solutions or posttreatment	NMR					
		$[\text{PtCl}_6]^{2-}$		$[\text{PtCl}_5(\text{OH})]^{2-}$		$[\text{PtCl}_6]^{2-}/[\text{PtCl}_5(\text{OH})]^{2-}$	
		δ_{Pt} , ppm ^a	lwhh, ppm ^b	δ_{Pt} , ppm ^a	lwhh, ppm ^b		
1	1.2	-4.3	1.4	644	5.7	1.2	
2	1.6	-5.1	1.3	645	7.5	4.5	
3	1.8	-3.7	1.2	653	5.4	6.5	
4	3.1	-0.8	1.4	658	5.4	7.3	
5	sample 2 after adding HCl	-5.9	1.2	643	8.2	0.52	
6	sample 2 after drying overnight and rewetting	-1.9	1.0	646	8.0	6.7	

^a With respect to δ_{Pt} for $[\text{PtCl}_6]^{2-}$ in the starting solutions. ^b lwhh = line width at half-height.

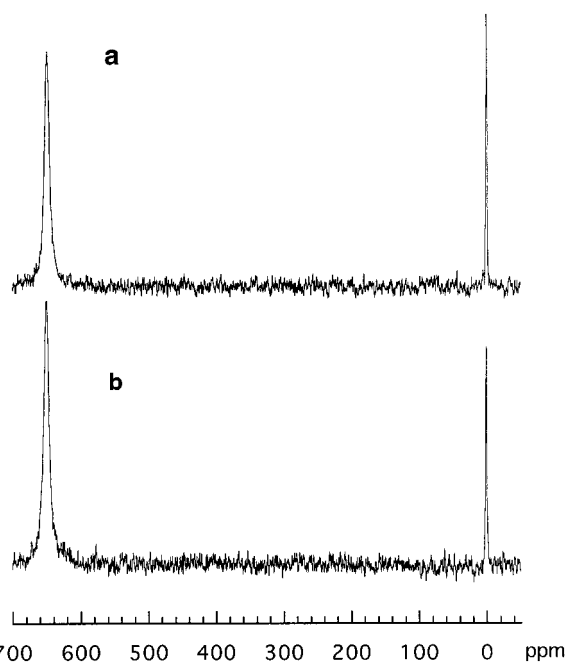


Figure 8. ^{195}Pt NMR of (a) a H_2PtCl_6 - Al_2O_3 mixture obtained by adding 1 g of Al_2O_3 to 20 mL of a 1.2×10^{-2} M H_2PtCl_6 solution at pH 1.6 and (b) after drying the mixture in (a) in a desiccator under vacuum overnight and rewetting the powder with 2 mL of distilled water.

temperature is apparently accompanied by further transformations of the adsorbed platinum species.

An attempt was made to detect ^{195}Pt MAS NMR signals from Sample 2 dried in a desiccator over P_2O_5 at room temperature for 2 weeks. However, no signal was detected for this sample even after accumulation overnight. This agrees with the data of ref 5 in which no Pt MAS NMR signal was observed from $\text{H}_2\text{PtCl}_6/\gamma\text{-Al}_2\text{O}_3$ at low Pt loadings after drying at 120 °C.

Discussion

^{195}Pt NMR of H_2PtCl_6 Solutions. As far as we know, no attempt has been previously made to systematically study Pt speciation in aqueous H_2PtCl_6 solutions as a function of pH and time of hydrolysis with ^{195}Pt NMR spectroscopy or other spectroscopic techniques. This lack of interest is surprising taking into account that the first studies on this system with macroscopic techniques date back to the early 1900s. We considered this study as a preliminary and necessary step in

investigating initial stages of platinum adsorption on alumina, since the pH values of impregnating H_2PtCl_6 solutions and, correspondingly, the compositions of the Pt complexes change considerably when alumina is brought into contact with H_2PtCl_6 solutions.

Assuming that protonation/deprotonation reactions 7–9 are fast on the NMR time scale, our ^{195}Pt NMR results qualitatively agree with the scheme of hydrolysis and deprotonation 5–9 proposed earlier in the literature.^{2,4} Five of the six platinum species that can be formed by reactions 5–9 are directly identified in the NMR spectra by their Pt chemical shift: $[\text{PtCl}_6]^{2-}$, $[\text{PtCl}_5(\text{H}_2\text{O})]^-$, $[\text{PtCl}_5(\text{OH})]^{2-}$, $[\text{PtCl}_4(\text{H}_2\text{O})_2]$, and $[\text{PtCl}_4(\text{OH})_2]^{2-}$ (Table 3). Moreover, on the basis of the best fits of the δ_{Pt} (tetrachloroplatinates) vs pH dependence, the chemical shift for $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$ complex, which cannot be directly identified in the NMR spectra, was calculated for the first time.

The Pt chemical shifts measured in this study for pentachloroplatinates are in fairly good accord with the literature data of Table 1. However, for tetrachloroplatinates, the agreement is not so good, since we did not observe the peaks of corresponding trans and cis isomers and suggest that they are closely spaced.

It is of interest to compare the distributions of chloroaqua and chlorohydroxo complexes in H_2PtCl_6 solutions as a function of pH measured directly by ^{195}Pt NMR in this study with those calculated by Mang et al.³ on the basis of reported equilibrium constants for reactions 5–9. A marked disagreement, both qualitative and quantitative, between the two series of data is evident. This can be illustrated by the following two examples.

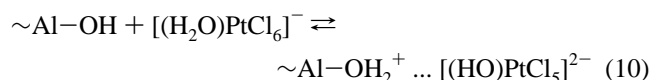
(i) No $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ or $[\text{PtCl}_4(\text{H}_2\text{O})_2]$ is predicted by the calculations at pH < 1.5, $\text{H}_2[\text{PtCl}_6]$ and $\text{H}[\text{PtCl}_6]^-$ being the major species.³ Actually, both aqua complexes were detected by ^{195}Pt NMR, $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ being very abundant (Figures 1 and 2).

(ii) In the pH interval of 4.0–6.0, $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^-$ is supposed to be the major species. Although this complex cannot be observed by NMR, it is certainly not the majority species, since the total fraction of tetrachloroplatinates is much smaller than that of pentachloroplatinates.

Most likely, such inconsistencies are due to the fact that the equilibrium constants for reactions 5–9 available in the literature and used for calculations in ref 3 are partly incorrect.

Mechanism of Platinum Adsorption on Alumina. Let us first discuss possible mechanisms of platinum adsorption on alumina from H_2PtCl_6 solutions. Most likely, $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{OH})]^{2-}$ are fixed on the positively charged surface of the wet solids by electrostatic interaction with the protonated OH groups as depicted by reaction 1 (see Introduction). Therefore, the chemical shifts of adsorbed Pt species are very close to those of known complexes in solutions. In view of the high specificity of Pt chemical shifts, this, probably, means that the coordination sphere of Pt is unaffected by adsorption.

The absence of an NMR signal corresponding to $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ bonded to protonated surface hydroxyls, which one may expect to find around $\delta_{\text{Pt}} = 504$ ppm, indicates fast deprotonation of the water ligand. It can occur by interaction with alumina surface hydroxyls:



Such deprotonation seems to be quite probable owing to the high proton affinity of alumina hydroxyls. According to

Contescu et al.,^{34,35} several structural types of surface hydroxyls are present on alumina, which differ considerably in their acid–base properties. The logarithms of the proton affinity constants for the most basic alumina hydroxyls [(Al_{Td})–OH] and [(Al_{Oh})–OH], where Al_{Td} and Al_{Oh} stand for tetrahedrally and octahedrally coordinated Al atoms, fall in the range of 6.6–7.0 and 9.6–10.0, respectively. The high proton affinity of these groups may provide fast deprotonation of [PtCl₅(H₂O)][–] upon contact of an H₂PtCl₆ solution with alumina.

Another plausible assumption is that local pH values higher than those in the corresponding bulk solutions can be achieved within a thin layer near the surface of alumina or inside the pores due to the formation of a positive surface charge by protonation of the OH groups. As we have recently outlined,³⁶ the double layer model then predicts a deficiency of protons and an excess of anions (including OH[–]) near the positively charged surface. It is a matter of debate if this effect is sufficient to account for complete deprotonation of [PtCl₅(H₂O)][–] to form [PtCl₅(OH)]^{2–} (reaction 7) followed by bonding of the latter species to the protonated surface hydroxyls. In our view, the occurrence of reaction 10 appears to be more probable.

In fact, eq 10 suggests that there is a specific interaction of the adsorbed [PtCl₅(OH)]^{2–} with some surface groups on the alumina. Experimentally, at the same time, the increased line widths of NMR resonances for adsorbed species indicate restricted mobility with respect to the bulk solution. This might appear contradictory with a model of electrostatic adsorption. Most likely, the answer is to be found in a triple-layer model, in which a part of the compensating anions is held in a plane close to the surface by forces weaker than chemical bond forces (electrostatic interaction and/or hydrogen bonding or, more generally, *outer-sphere* ligand bonding³⁶).

It should be emphasized that, whatever the mechanism of [PtCl₅(H₂O)][–] deprotonation, the ¹⁹⁵Pt NMR data clearly indicate that platinum speciation inside a thin layer in the vicinity of the positively charged alumina surface is different from that in the bulk solutions. A similar conclusion was drawn in refs 37 and 38 from a ⁹⁵Mo NMR study of γ -alumina impregnated with aqueous solutions of ammonium heptamolybdate at different initial pH values. The decomposition of Mo₇O₂₄^{6–} to form MoO₄^{2–} was found to occur due to the increase in the pH of the impregnating solution inside the pores of alumina as a result of protonation of the surface hydroxyls. The rise in pH caused the equilibrium 7MoO₄^{2–} + 8H⁺ = Mo₇O₂₄^{6–} + 4H₂O to shift to the left and MoO₄^{2–} to be formed.

Most of the Pt anions fixed on the surface by electrostatic interaction with the protonated OH groups cannot be removed by washing alumina with water, because the protons are strongly held on the alumina surface. This is in accord with the high proton affinities of surface hydroxyls³⁵ and agrees with the data of ref 39 which showed that only 5% of adsorbed MoO₄^{2–} or Mo₇O₂₄^{6–} could be removed by washing from alumina impregnated with an ammonium heptamolybdate solution at pH values below the PZC of alumina.

Parameters of ¹⁹⁵Pt NMR Spectra. The data of Table 4 clearly show that δ_{Pt} of the adsorbed Pt complexes is to some

(34) Contescu, C.; Jagiello, J.; Schwarz, J. A. *Langmuir* **1993**, *9*, 1754–1765.

(35) Contescu, C.; Contescu, A.; Schwarz, J. A. *J. Phys. Chem.* **1994**, *98*, 4327–4335.

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(39) Kasztelan, S.; Grimblot, J.; Bonnelle, J. P.; Payen, E.; Toulhoat, H.; Jacquin, Y. *Appl. Catal.* **1983**, *7*, 91–112.

extent dependent on the pH of the starting H₂PtCl₆ solutions. The δ_{Pt} of [PtCl₅(OH)]^{2–} tends to increase, and the δ_{Pt} of [PtCl₆]^{2–} tends to approach $\delta_{\text{Pt}} = 0$ ppm as the pH values of the starting solutions increase and, correspondingly, the positive charge of the alumina surface decreases. The effect of the δ_{Pt} shift is more pronounced for [PtCl₅(OH)]^{2–} ($\Delta\delta_{\text{Pt}} = 14$ ppm, Samples 1 to 4) and less certain for [PtCl₆]^{2–} due to possible drift of the magnetic field during the NMR measurements (the spectrometer was operated in the unlocked mode).

The relatively small line widths in the NMR spectra of adsorbed [PtCl₆]^{2–} and [PtCl₅(OH)]^{2–} (Table 4) are quite remarkable. They are comparable to those in frozen aqueous solutions of H₂PtCl₆.⁴⁰ We carried out variable-temperature NMR experiments showing that the [PtCl₆]^{2–} and [PtCl₅(H₂O)][–] lines in frozen solutions cooled to 253, 233, or 213 K are only slightly broaden: the line width at half-height (lwhh) of both signals increased from 0.7 ppm for the liquids to ~3.5 ppm for the solids. This indicates that the loss of mobility has only a small effect on the NMR line widths because of relatively small chemical shift anisotropy of octahedral Pt(IV) complexes and agrees with the ¹⁹⁵Pt NMR data under static conditions for powder K₂PtCl₆.¹⁸ No significant difference between the lwhh of [PtCl₆]^{2–} and [PtCl₅(H₂O)][–] was found for the frozen solutions. In contrast to this, the NMR line of adsorbed [PtCl₅(OH)]^{2–} is markedly broader than that of adsorbed [PtCl₆]^{2–} (Table 4). This can be rationalized by assuming a higher chemical shift anisotropy for the adsorbed [PtCl₅(OH)]^{2–} complex caused by perturbation of its ligand sphere upon adsorption.

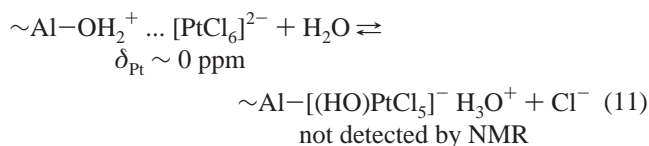
From Electrostatic Adsorption to Grafting. The next point to be discussed is the *reversible* disappearance of the NMR signals of adsorbed platinum species after the removal of surface water at room temperature and the reappearance of the signals upon rewetting of the solid. One hypothesis is that these effects may be associated with relaxation phenomena. For instance, we might assume that adjacent protons from water can provide an efficient relaxation mechanism for ¹⁹⁵Pt by ¹H–¹⁹⁵Pt coupling. The removal of these protons upon drying would result in increasing the *T*₁ relaxation time to such an extent that the signal is saturated in a few accumulations and thus becomes unobservable.

Alternatively, we may suggest that removal of physisorbed water and destruction of the electrical double layer upon drying would allow the adsorbed platinum anions to approach the positively charged surface more closely. This would result in stronger perturbation of their ligand spheres and, consequently, in the growth of chemical shift anisotropy due to increasing polarization effects. For dried solids, the chemical shift anisotropy may increase to such an extent that the signals from adsorbed platinum complexes become unobservable by static NMR because of heavy line broadening. Even under the conditions of our MAS NMR experiments, the chemical shift anisotropy averaging was not sufficient to allow the detection of the adsorbed platinum species. After rewetting the solids, the layer of physisorbed water is restored, and the NMR signals reappear. Since no change in the positions and relative intensities of the [PtCl₆]^{2–} and [PtCl₅(OH)]^{2–} signals was found to occur after water removal at 20 °C and rewetting (Figure 8), we may conclude that, at this stage of catalyst preparation, a major part of the adsorbed platinum species remains intact.

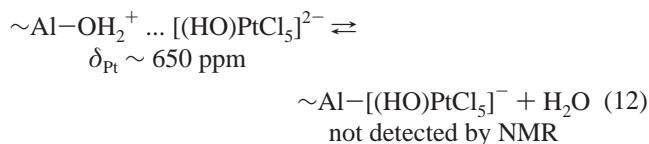
In contrast, *irreversible* disappearance of the NMR signals after drying at 90 °C might indicate a modification of the symmetry of the original octahedral Pt complexes to give rise

(40) Thouvenot, R.; Shelimov, B. Unpublished results.

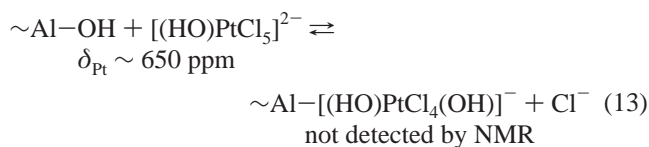
to a species of a lower symmetry and higher chemical shift anisotropy, which cannot be detected by static NMR. Such species may result from a ligand exchange of $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{OH})]^{2-}$ with the surface OH groups as depicted by reaction 3 in the Introduction and, more precisely, by the following reactions:



(grafting of hexachloroplatinates), and



or alternatively



These reactions may or may not be followed by deprotonation of the bridging OH group as shown by reaction 4. That a major change occurs in the Pt(IV) coordination sphere is confirmed by our EXAFS results which will be reported in detail in another publication.

Due to stronger bonding of the ligand-exchanged complexes to the surface, the initial adsorbed platinum complexes cannot be regenerated by treating the solid with water at room temperature.

Conclusions

The present work clearly demonstrates the potential of ^{195}Pt NMR spectroscopy both for identifying platinum complexes in aqueous H_2PtCl_6 solutions and for studying the initial stages of Pt deposition on alumina from these solutions, i.e., for investigating platinum complex speciation at the liquid–solid interface.

Applying ^{195}Pt NMR to aqueous H_2PtCl_6 solutions at different initial pH values made it possible to reliably identify a number of hexa-, penta-, and tetrachloroplatinate complexes by their ^{195}Pt chemical shift (δ_{Pt}), thus confirming the occurrence of aquation reactions in H_2PtCl_6 solutions proposed earlier in the

literature. The acid dissociation constants ($\text{p}K_{\text{a}}$) for monoqua and diaqua complexes were determined from the δ_{Pt} dependences on pH of the H_2PtCl_6 solutions. It is also shown that the published quantitative treatments of these equilibria (equilibrium and acid dissociation constants) are only partly correct.

More importantly, ^{195}Pt NMR of $\text{H}_2\text{PtCl}_6\text{--Al}_2\text{O}_3$ mixtures allowed us, *for the first time*, to observe adsorbed $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{OH})]^{2-}$ anions on the positively charged surface of wet alumina. A small difference in δ_{Pt} for the adsorbed and liquid-phase $[\text{PtCl}_6]^{2-}$ points to only slight perturbation of the Pt atom coordination sphere in the adsorbed species which are likely held by electrostatic interaction in the Stern layer. Unlike in H_2PtCl_6 solutions, complete deprotonation of $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ to $[\text{PtCl}_5(\text{OH})]^{2-}$ occurs at the alumina–solution interface, presumably via direct interaction of the aqua complex with basic alumina hydroxyls. The $[\text{PtCl}_5(\text{OH})]^{2-}(\text{ads})/[\text{PtCl}_6]^{2-}(\text{ads})$ ratio rises with increasing pH of the impregnating solution and decreases upon adding HCl when the adsorption is completed. Thus, the composition of adsorbed platinum complexes in unreduced Pt/ Al_2O_3 catalysts can be efficiently controlled by adjusting the pH values of H_2PtCl_6 solutions and/or by acidifying alumina with adsorbed Pt complexes. However, more studies are necessary to learn whether the Pt complex composition would have an effect on the evolution of adsorbed species upon calcination and on the Pt metal dispersion after reduction.

The $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{OH})]^{2-}$ signals disappear after removal of physisorbed water at room temperature and reappear upon rewetting the powder. It is suggested that the reversible disappearance of the NMR signals is associated with an increase of chemical shift anisotropy for the Pt complexes when they approach the positively charged surface of the dry solid. The drastic irreversible decrease in the NMR signal intensity after drying Pt/ Al_2O_3 at 90 °C is presumably related to the formation of adsorbed platinum complexes with a lower symmetry and higher chemical shift anisotropy which escape NMR detection. Such species probably arise from ligand-exchange reactions of Cl^- ligands with the surface OH groups and further deprotonation of the bridging hydroxyl, i.e., as a result of grafting to the alumina surface.

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