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^{195}Pt NMR Study of the Speciation and Preferential Extraction of Pt(IV)–Mixed Halide Complexes by Diethylenetriamine-Modified Silica-Based Anion Exchangers

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A detailed ^{195}Pt NMR study of the distribution of Pt(IV) complex species resulting from the aquation of H_2PtCl_6, H_2PtBr_6, and mixtures of H_2PtCl_6/H_2PtBr_6 in water/dilute $HClO_4$ has been carried out to obtain an understanding of the speciation in these solutions as relevant to the recovery of Pt(IV) complexes from process solutions. A species distribution plot of the $[PtCl_6]^{2-}$, $[PtCl_5(H_2O)]^-$, and $[PtCl_4(H_2O)_2]$ shows that in equilibrated, relatively concentrated H_2PtCl_6 solutions ($[Pt]_t > 0.12$ M), the $[PtCl_4(H_2O)_2]$ species is below the ^{195}Pt NMR detection limit; for $[Pt]_t$ concentrations < 0.1 M, the relative concentrations of the $[PtCl_5(H_2O)]^-$ and $[PtCl_4(H_2O)_2]$ species increase significantly, as a result of relatively rapid aquation of the $[PtCl_6]^{2-}$ and $[PtCl_5(H_2O)]^-$ complexes under these conditions. From this ^{195}Pt NMR data the aquation constants of $[PtCl_6]^{2-}$ and $[PtBr_6]^{2-}$ of $\log K_6 \approx 1.75 \pm 0.05$ and $\log K_6 \approx 2.71 \pm 0.15$, respectively, have been determined at 30 °C. In mixtures of H_2PtCl_6/H_2PtBr_6 in water, a number of previously unidentified aquated complexes of the general formula $[PtCl_{5-n}Br_n(H_2O)]^-$ ($n = 0$–5) could be identified, including the possible geometrical isomers of these complexes. These ^{195}Pt NMR assignments were confirmed by remarkably systematic, linear relationships between the ^{195}Pt chemical shift increments induced by substitution of Cl^- ions by n Br^- ions in $[PtCl_{6-n}Br_n]^{2-}$ and $[PtCl_{5-n}Br_n(H_2O)]^-$ complexes. Preferential extraction of the $[PtX_6]^{2-}$ (X = Cl, Br, or a mixture of the two halides) species over their corresponding aquated $[PtX_5(H_2O)]^-$ counterparts by silica-based diethylenetriamine anion exchangers could be demonstrated by means of ^{195}Pt NMR spectroscopy.

Introduction

The production of the platinum group metals (PGMs; Pd, Pt, Rh, Ir, Ru, and Os) has grown significantly over the last few decades as a result of their increased demand in a wide variety of applications, of which the use of Pt, Pd, and Rh in automobile exhaust emission control catalysts is probably the most important.[1,2] A crucial and complex part in the production of the PGMs is their efficient separation during the refining stages from halide-rich acidic process streams. To this end, "classical" refining techniques were largely applied until the mid 1970s, involving numerous and often rather unselective precipitation and dissolution steps.[3,4] Recently more efficient and selective extraction processes involving solvent extraction, anion exchange, and even methods of "molecular recognition" have found large-scale application in the separation and refining of the PGMs.[4-6]

In highly acidic chloride-rich aqueous process solutions, the PGMs therefore predominantly exist as stable anionic, relatively kinetically inert metal chloride complexes of the type $[MCl_x]^{n-x}$, where M is the metal, n is the oxidation state of the metal, and x is typically 4 or 6.[7,8] Most separation processes under these conditions generally require selective

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transfer of $[MCl_x]^{n-x}$ species (for any particular PGM complex) from an aqueous to a nonaqueous phase, of which, in the case of Pd(II) and Pt(IV), the $[PdCl_4]^{2-}$ and $[PtCl_6]^{2-}$ anions are generally the most readily extracted.[2]

Dependent on the solution conditions, the $[MCl_x]^{n-x}$ complexes may undergo varying degrees of aquation and/or hydrolysis (or deprotonation) reactions, leading to several $[MCl_{x-y}(H_2O)_y]^{n-x+y}$ and $[MCl_{x-z}(OH)_z]^{n-x}$ species in solution (with $n = 2-4$, $x = 4$ or 6, and y, $z = 0-6$).[9] The acidity, temperature, chloride and PGM concentrations, and the "age" of the solutions generally determine the extent of aquation and hydrolysis.[8] The identification of the various PGM-chloro and mixed chloro-aqua species was largely undertaken in the 1960−1970s by means of electronic UV−vis absorption spectrophotometry based on intensity and the wavelength maxima differences for the complex species as exemplified by the studies of Elding and others[10,11] and reviewed by Simanova.[9] These studies suggest that, depending on the Cl^- concentration, as the pH of the solutions increases, a complicated mixture of species such as $[MCl_{x-y-z}(H_2O)_y(OH)_z]^{n-x+y}$ and $[MCl_{x-z}(OH)_z]^{n-x}$ may result, importantly, at differing rates for the individual PGM ions.[9] Moreover in the context of selective extraction and separation of, for example $[MCl_6]^{2-}$, the corresponding $[MCl_{x-y}(H_2O)_y]^{n-x+y}$ species (or their hydrolysis products) are thought to be much less readily extractable, particularly those derived from Rh(III) and Ir(III). Clearly, inadequate understanding of the speciation of PGM complexes in process solutions leads to poor control, which can result in significant loss of efficiency in the recovery of these precious metals.[2,8,12,13] A vital aspect for efficient PGM separation and recovery is a detailed knowledge of PGM speciation under variable conditions in process solutions which may lead to higher separation efficiency. Of the several publications on PGM−halide extractions into water immiscible solvents, few have adequately addressed the question of speciation of Pt(IV) complexes potentially present in process solutions of interest, not to mention a detailed examination of the effect speciation on the relative extractabilities of these.[10,12,14,15] Moreover in most cases, the UV−vis spectrophotometry used to monitor extraction from solution is not entirely satisfactory in this context because of the inherently low resolution and significant spectral overlap of absorption spectra of PGM complexes.

^{195}Pt NMR spectroscopy is a high-resolution spectroscopic method with which to examine the speciation of, in particular, Pt(IV) complexesbecause the ^{195}Pt isotope has a natural abundance of 33.7% and an NMR receptivity of 19.1 relative to ^{13}C, and spectra are thus readily obtainable.[16] The extremely large ^{195}Pt chemical shift range ($\delta^{195}Pt > 13\,000$ ppm), together with the high sensitivity of ^{195}Pt shieldings to oxidation state and inter alia the detailed structure of the complex in solution, makes ^{195}Pt NMR an excellent tool for speciation studies in this context.[17,18,19] Moreover, as has recently been shown, ^{195}Pt NMR together with advanced density functional theory (DFT) and molecular dynamics calculations is a good probe for the solvation/hydration shells of the anionic complexes $[PtCl_6]^{2-}$, $[PtCl_4]^{2-}$, $[PdCl_4]^{2-}$, and $[RhCl_6]^{3-}$, as well as demonstrating ion-pairing between $[PtCl_6]^{2-}$ and Na^+ in methanol solutions.[20] To our knowledge very little published work on the use of ^{195}Pt NMR to study extractions of Pt−halides exists, apart from one study more than two decades ago on the use of ^{195}Pt NMR in an extraction study of Pt(IV) complexes by octylaniline.[21]

We here report a detailed ^{195}Pt NMR study of the species distribution of H_2PtCl_6, H_2PtBr_6, and a mixture of the latter two Pt(IV) salts in acidic water solutions, with reference to their relative extractability by a silica-based (poly)amine-containing anion exchanger as model system, based on our recent findings that these silica-based diethylenetriamine-containing anion exchangers may be used as efficient and selective materials for Pt(IV) and Pd(II) chloro complex recovery from authentic industrial process solutions from highly acidic, chloride-rich solutions.[22,23] In this study, we attempted to simulate conditions approximating industrial process solutions, under which the immobilized amine groups are essentially protonated, so that the material functions as an anion exchanger, for which extraction is based on the substitution of Cl^- by anionic $[MCl_x]^{n-x}$ complexes (eq 1).[7,8]

$$(x-n)R_3NH^+Cl^- + [MCl_x]^{n-x} \rightleftharpoons R_3NH^+{}_{x-n}[MCl_x]^{n-x} + (x-n)Cl^- \quad (1)$$

Conveniently, the total concentrations of platinum(IV) in solution ($[Pt]_t$) required to rapidly acquire good ^{195}Pt NMR

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spectra (roughly 0.05−0.5M) which approximately match concentrations of the order of 10−100 g/L, common in industrial process solutions.[4,6,24] We focused on the extraction of Pt(IV) chlorides and bromides and mixtures thereof, since the presence of Pt(II) halides in relatively oxidizing process solutions is unlikely.

Experimental Section

Reagents. Platinum salts $H_2PtCl_6 \cdot H_2O$ (Aldrich) and H_2PtBr_6 (Johnson Matthey PLC, Precious Metals Division) were of reagent grade quality and were dried in vacuo and stored in a desiccator prior to use. Aqueous solutions were prepared using ultrapure Milli-Q water (MQ, >18 MΩ). The ion exchanger **1**, prepared as reported elsewhere,[22] contained a diethylenetriamine functional group grafted onto silica (Aldrich silica gel Davisil, particle size = 35−60 mesh (250−500 μm), surface area = 480 m^2/g, pore volume = 0.75 cm^3/g) with a ligand concentration of 0.93 mmol g^{-1}.

^{195}Pt NMR Spectroscopy. ^{195}Pt NMR spectra were recorded at 303 K using a Varian INOVA 600 MHz spectrometer operating at 129 MHz for ^{195}Pt, using a 5 mm broad-band probe. A 1 mm coaxial insert tube containing a $[PtCl_6]^{2-}$ reference solution ($\delta^{195}Pt = 0.0$) (500 mg cm^{-3} $H_2PtCl_6 \cdot H_2O$ in 30% v/v D_2O/1 M HCl) was inserted into 5 mm NMR tubes. Because of the wide range of ^{195}Pt chemical shifts, spectral widths of 200−250 kHz were used, corresponding to 1500 to 2000 ppm. T_1 relaxation times were measured for all peaks, and acquisition times were chosen such that the integrated peak areas of all ^{195}Pt resonances were essentially proportional to the complex concentration. A line-broadening factor of 20 Hz was applied, and the effective line-width at half-height for different species ranged from 40 to 80 Hz; the measured $\delta^{195}Pt$ values are estimated to an accuracy of ± 1 ppm. Quantification of the Pt extraction, as well as the determination of the relative concentrations of Pt(IV) species present in solution, was performed by comparison of the integral peak areas of the individual peaks to the peak area of the $[PtCl_6]^{2-}$ insert; the maximum experimental error for the peak area determination (and thus relative species concentration) is estimated to be 5−10% relative.

Extraction Experiments. Before they were put in contact with ion exchanger **1**, all solutions had been aged until no further changes in species distributions were observed in the ^{195}Pt NMR spectra. In the pure H_2PtCl_6/H_2PtBr_6 solutions, no peak distribution changes could be detected after the first measurement (<10 min after dissolution), whereas a steady state after the mixing of equimolar solutions of H_2PtCl_6 and H_2PtBr_6 was reached only after ~5 h. As a precaution, all solutions were aged for at least 24 h before being put into contact with the ion exchange material. Since it is known that the rate of aquation of aqueous solutions of Pt(II/IV) halides is enhanced when irradiated with light of a specific wavelength,[25,26] the potential contribution of surrounding light under our experimental conditions on the extent of aquation was tested. Aqueous solutions of H_2PtCl_6 of varying concentrations were illuminated in glass containers for several hours using a 150 W quartz−halogen lamp from a conventional slide projector as a light source (spectral range of ~310−900 nm). The species distribution obtained for the illuminated solutions was identical to similar solutions kept in the dark. The effect of ambient light, of much lower in intensity, was thus assumed to be negligible, and the solutions were stored without the exclusion of light.

A 100 mg portion of **1** was added to a vial containing 2000 μL of a 0.48 M $H_2PtCl_6 \cdot H_2O$ or H_2PtBr_6 solution in water (or in 0.12 M $HClO_4$ for the mixture of the two Pt(IV) salts); the suspension shaken for 60 ± 5 s, after which the supernatant and loaded ion exchanger were separated, and 400 μL of supernatant was transferred into an NMR tube for ^{195}Pt NMR spectroscopy. The total time between addition of **1** and the start of the measurement was ~3.5 min. Consecutive portions of 100 mg of **1** were added to ensure an excess of total platinum to ligand molecules throughout all extractions because the aim of the study was to observe possible *relative differences in the extractability* of the Pt(IV) species rather than to achieve *maximum extraction*. Additions were performed until the total platinum concentration ($[Pt]_t$) was too low for a ^{195}Pt resonance to be detected, which generally occurred after 600−700 mg of **1** had been added. After each addition of ion exchanger, ^{195}Pt NMR spectra were recorded several times to monitor possible speciation changes in time. When no more significant changes were observed in the solution, the next portion of **1** was added.

Results and Discussion

Speciation in Aqueous H_2PtCl_6 Solutions. The strong acid H_2PtCl_6 readily dissociates in water,[27] and $[PtCl_6]^{2-}$ undergoes partial aquation forming the corresponding monoaqua and diaqua species (eq 2a and b)[25,27,28]

$$[PtCl_6]^{2-} + H_2O \rightleftharpoons [PtCl_5(H_2O)]^- + Cl^- \qquad K_6 = [PtCl_6]^{2-}/[PtCl_5(H_2O)]^-[Cl] \tag{2a}$$

$$[PtCl_5(H_2O)]^- + H_2O \rightleftharpoons [PtCl_4(H_2O)_2] + Cl^- \qquad K_5 = [PtCl_5(H_2O)]^-/[PtCl_4(H_2O)_2][Cl] \tag{2b}$$

where K_6 and K_5 are the usual stability (or equilibrium) constants for the reverse reaction.[29] The few reported values for log K_6 vary significantly from 1.47 to 2.2,[9] presumably because they were determined at temperatures between 25 and 60 °C and at different ionic strengths; only one reported value of log $K_5 \approx 3.70$ is available in the literature.[9] The chloroaqua platinum(IV) complexes behave like weak acids and are found to undergo hydrolysis upon increasing pH,[27,30] according to eq 3, where K_a is the acid dissociation constant

$$[PtCl_5(H_2O)]^- \rightleftharpoons [PtCl_5(OH)]^{2-} + H^+ \qquad K_a = [PtCl_5(OH)]^{2-}[H^+]/[PtCl_5(H_2O)]^- \tag{3}$$

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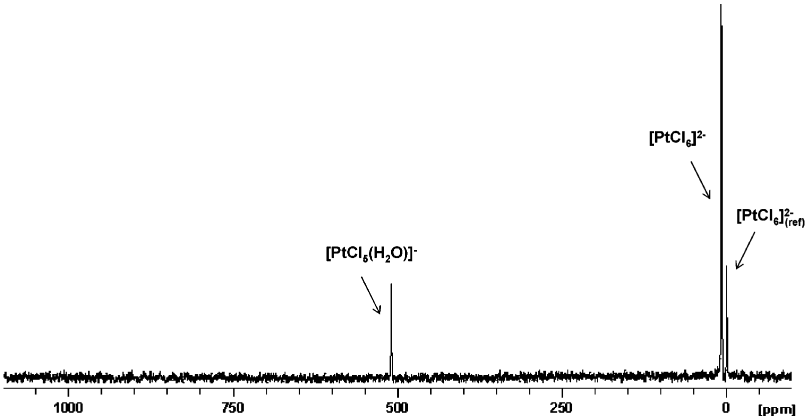

Figure 1. ^{195}Pt NMR spectrum of an aqueous solution (0.48 M) of H_2PtCl_6.

Since the reported pK_a value for the deprotonation of $[PtCl_5(H_2O)]^-$ is ~3.5[30] and the solutions at our working conditions (0.48 M Pt) were fairly acidic (pH of ~1), hydrolysis is not expected to play a role. This is confirmed by the ^{195}Pt NMR spectrum of an aged aqueous 0.48 M solution of $H_2PtCl_6 \cdot H_2O$ in which the only two observable species present are, $[PtCl_6]^{2-}$ at 8 ppm and $[PtCl_5(H_2O)]^-$ at 510 ppm (Figure 1). The small downfield displacement of ~8 ppm in $\delta^{195}Pt$ for the $[PtCl_6]^{2-}$ peak to the external reference $[PtCl_6]^{2-}{}_{ref}$, for which $[Pt]_t \approx 1.17$ M in a 1 M HCl solution, emphasizes the sensitivity of the ^{195}Pt chemical shift of a particular complex to small differences in concentration, pH, and solvent composition on the ^{195}Pt chemical shift. (In the literature, different reference solutions under variable conditions of temperature, concentration, and solvent composition lead to discrepancies of reported $\delta^{195}Pt$ values of several parts per million, greater than the ±1 ppm value established in our study at 303 K using the same internal reference solution.) The observed chemical shift difference ($\Delta(\delta^{195}Pt)$) of 502 ppm between $[PtCl_5(H_2O)]^-$ and $[PtCl_6]^{2-}$ of the pentachloroaqua species is in good agreement with previously reported values.[30,31]

Interestingly, in our solutions, the relative concentration (as measured by integrated peak intensity) of $[PtCl_5(H_2O)]^-$ was found to be between 18 and 20% of the total concentration of the Pt complexes, which is considerably lower than that reported in spectra by Shelimov et al., in which the concentration of $[PtCl_5(H_2O)]^-$ appears to be closer to 50%.[30] Moreover, these authors reported the presence of the $[PtCl_4(H_2O)_2]$ species at 1005 ppm relative to $[PtCl_6]^{2-}$ in an acidic (pH 1.35) solution for which $[Pt]_t$ was ~ 66 mM. In our aged, fairly concentrated solutions (0.48 M H_2PtCl_6), no peak attributable to this complex could be detected, suggesting a concentration dependence of the Pt(IV) species distribution. Since no quantitative species distribution data of H_2PtCl_6 in water could be found in the literature, we examined the dependence of the relative amount of $[PtCl_{6-n}(H_2O)_n]^{n-2}$ species for different $[Pt]_t$ in equilibrated solutions, which clearly shows that the degree of aquation increases with decreasing total H_2PtCl_6 concentration at 30 °C (Figure 2). Evidently, the equilibrium reactions (eq 2a and b) are driven to the right for lower $[Pt]_t$ as a result of the mass action effect of water, confirmed by the emergence of the additional peak at 1006 ppm assigned to $[PtCl_4(H_2O)_2]$ in a $[Pt]_t \approx 65$ mM solution, with the concomitant decrease of the relative concentration of $[PtCl_6]^{2-}$, shown in Figure 2. In our most dilute solution ($[Pt]_t \approx 6$mM), the peak from $[PtCl_4(H_2O)_2]$ contributes to almost 10% of all the observable Pt species. Analysis of the species distribution pattern corresponds to an average log K_6 value (eq 2a) of 1.75 ± 0.05 (calculated at 30 °C, without ionic strength control); the agreement of this value with the published value of log $K_6 = 1.49$ is reassuring in light of the fact that the latter was established under somewhat different conditions and at a higher temperature (50 °C).[32] Qualitatively, we found the equilibrium of eq 2a to be sensitive to the temperature (data not shown here) and that the relative extent of aquation was found to increase with increasing temperature, consistent with lower log K_6 values.

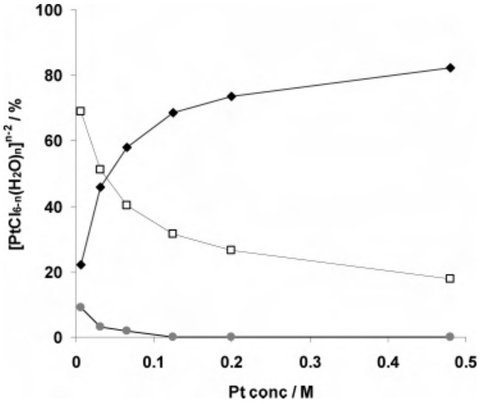

Figure 2. Relative amounts (in %) of $[PtCl_6]^{2-}$ (marked ♦), $[PtCl_5(H_2O)]^-$ (□), and $[PtCl_4(H_2O)_2]$ (●) species in aqueous solutions as a function of different H_2PtCl_6 concentrations. (Solutions were aged to steady state before spectra were recorded.)

In our ^{195}Pt NMR spectra, resonances of both $[PtCl_6]^{2-}$ and $[PtCl_5(H_2O)]^-$ shift downfield by generally less than 5 ppm with decreasing $[Pt]_t$. These changes are predominantly the result of a small increase in pH upon dilution, since no

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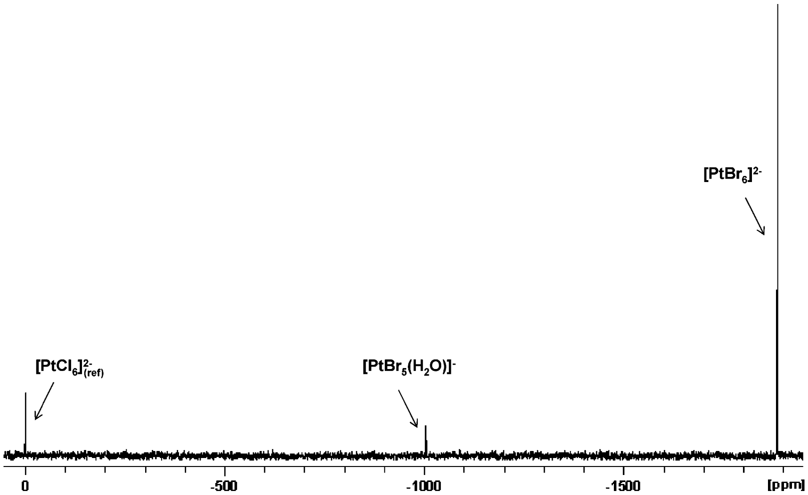

Figure 3. ^{195}Pt NMR spectrum of an aqueous solution (0.48 M) of H_2PtBr_6.

such changes to δ^{195}Pt are seen for changes in $[Pt]_t$ concentration at constant acidity. By contrast, the δ^{195}Pt of the resonance assigned to $[PtCl_4(H_2O)_2]$ shows an appreciable downfield shift with decreasing $[Pt]_t$, changing from 1006 ppm at 65 mM to 1052 ppm at 6 mM. This may be the result of the much lower pK_{a1} value for the first hydrolysis of $[PtCl_4(H_2O)_2]$, estimated to be between 1.9 and 2.7.[30,33] As a consequence, in the 6 mM solution, at a pH of ∼1.9, the $[PtCl_4(H_2O)_2]$ complex will probably coexist in fast exchange on the NMR time scale with $[PtCl_4(OH)(H_2O)]^-$, which has an estimated limiting δ^{195}Pt of 1176 ppm,[30] thereby accounting for the marked concentration dependence of the chemical shift of the resonance for $[PtCl_4(H_2O)_2]$.

In this study, we monitored our solutions for changes in the intensities and distribution of ^{195}Pt signals after each dilution. Interestingly, whereas the composition of the more concentrated solutions ($[Pt]_t > 0.1$ M) did not undergo noteworthy changes after the first measurement (within 10 min after dilution), small increases in the concentrations of aquated species could be observed for several hours after dilution, particularly for the most dilute (in $[Pt]_t$) solutions. This suggests not only that the extent and rate of the aquation reactions in eq 2 is concentration dependent but implies that the rate of aquation in the more concentrated solutions appears to be too fast to be measurable by means of ^{195}Pt NMR spectroscopy, given the time required to record δ^{195}Pt FT-NMR spectra. This observation is at variance with the generally espoused viewpoint that ligand exchange in Pt(IV) complexes is *always* very slow[9,32,34] but suggests that relative rates of aquation or anation (anation refers to halide ion coordination of an aquated Pt(IV) species, i.e. the reverse of eq 2a or b) for this Pt(IV) system in solution depend appreciably on the $[Pt]_t$ particularly when measured on the NMR time scale.

We find no ^{195}Pt NMR evidence of the existence of a possible binuclear $[Pt_2Cl_{10}]^{2-}$ or $[Pt_2Br_{10}]^{2-}$ anion[35] (see the next section) in our aqueous solutions; all detectable ^{195}Pt NMR resonances within the wide spectral windows examined in this study (+1800 to −2000 ppm) can be fully assigned to the mononuclear Pt(IV) complexes (vide infra). Moreover, the binuclear $[Pt_2X_{10}]^{2-}$ (X = Cl or Br) anions which have been reported were isolated from nonaqueous media, under conditions very different from those pertaining to our relatively dilute aqueous solutions.[35] It is thus reasonable to conclude that in aqueous media at our working $[Pt]_t$ concentrations the binuclear $[Pt_2X_{10}]^{2-}$ anions either do not exist in our solutions or are present at a level well below the limits of detection of high-field ^{195}Pt NMR spectroscopy.

Speciation in Aqueous H_2PtBr_6 Solutions. Similar to the hexachloroplatinum(IV) anion, $[PtBr_6]^{2-}$ is prone to undergo aquation upon dissolution of H_2PtBr_6 in water. In contrast to $[PtCl_6]^{2-}$, only the first aquation step (eq 4, with a reported log $K_6 = 2.85$)[32] is significant under our experimental conditions, since no evidence was found in the literature, as well as from our own experiments, of any second aquation step resulting in $[PtBr_4(H_2O)_2]$ taking place in aqueous solutions of $[PtBr_6]^{2-}$.[32,36]

$$[PtBr_6]^{2-} + H_2O \rightleftharpoons [PtBr_5(H_2O)]^- + Br^-$$
$$K_6 = [PtBr_6]^{2-}/[PtBr_5(H_2O)]^-[Br] \quad (4)$$

The ^{195}Pt NMR spectrum of a solution of H_2PtBr_6 in water (0.48 M) is dominated by the peak of $[PtBr_6]^{2-}$ at −1882 ppm (Figure 3) with a second peak at δ^{195}Pt = −1003 ppm clearly visible, assigned to the $[PtBr_5(H_2O)]^-$ species on the basis of the following arguments: (i) when the H_2PtBr_6 solution is diluted, the relative integrated intensity of the peak at −1003 ppm increases significantly, tending toward some 25% at 25 mM $[Pt]_t$, with no other resonances being visible in the spectrum; (ii) addition of an equimolar amount of Br^- by "titration" (as dilute HBr solution) to the aqueous solution of H_2PtBr_6, results in the rapid disappearance of the peak at

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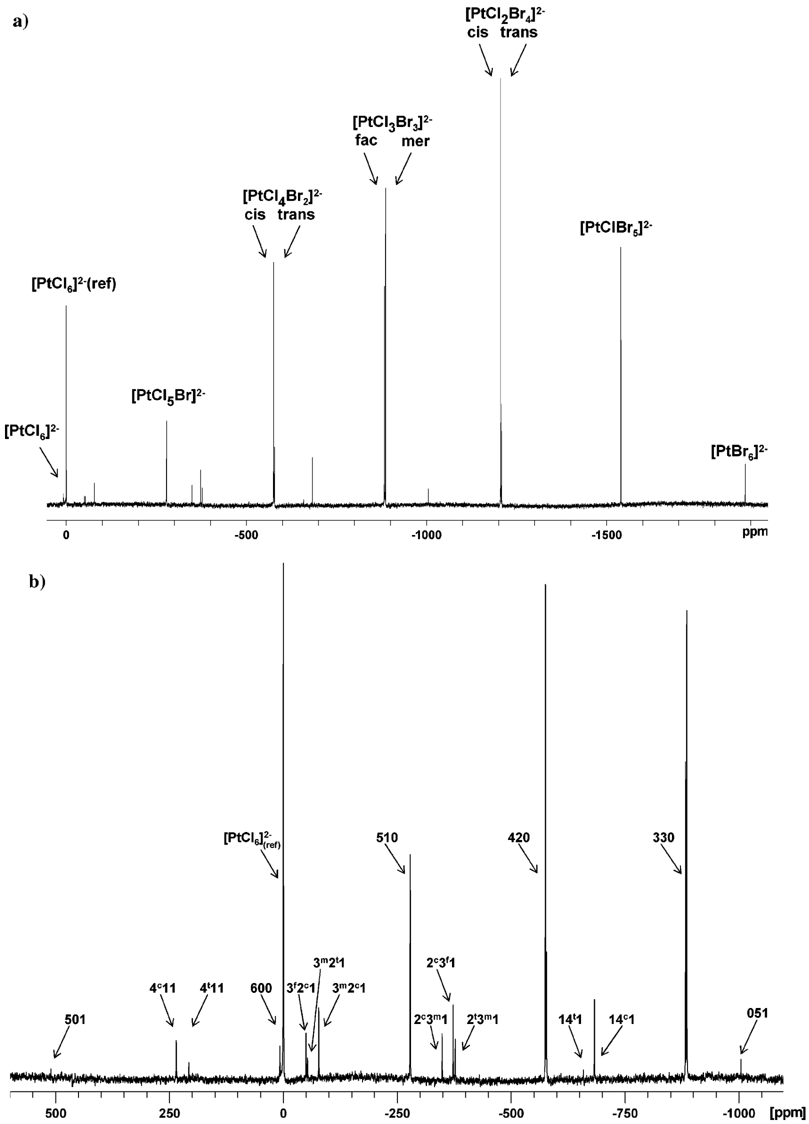

Figure 4. ^{195}Pt NMR spectra of (a) an equimolar solution (0.48 M) of a mixture of H_2PtCl_6 and H_2PtBr_6 in 0.12M $HClO_4$ (not shown is the signal of the **501** species, $[PtCl_5(H_2O)]^-$ at ca. +510 ppm) and (**b)** the same solution showing all the aquated $[PtCl_{5-n}Br_n(H_2O)]^-$ ($n = 0-5$) species.

−1003 ppm with a corresponding growth of the $[PtBr_6]^{2-}$ signal (similar Cl^- anation is observed when an aqueous H_2PtCl_6 solution is titrated with diluted HCl); and (iii) in view of the acidity (pH < 2) of the H_2PtBr_6 solution at our working conditions, the likelihood that the −1003 ppm signal is the result of a hydrolysis product such as $[PtBr_5(OH)]^{2-}$ is negligible, given the estimated pK_a value for this species of ~4.4.[32]

At the same total $[PtX_6]^{2-}$ ($X = Cl^-$ or Br^-) concentration of 0.48 M, the relative concentration in solution of $[PtBr_5(H_2O)]^-$ at 6% is significantly lower compared to the Pt−chloro system, with $[PtCl_5(H_2O)]^-$ at 18%, suggesting that the equilibrium of eq 4 lies more to the left than for eq 2a, as might be expected. A log K_6 value of $\sim 2.71 \pm 0.15$ (eq 4) is estimated from an analysis of the relative concentrations of the $[PtBr_6]^{2-}$ and $[PtBr_5(H_2O)]^-$ species in 0.48, 0.10, and 0.025 M solutions of H_2PtBr_6. This value agrees well with the log K_6 value of 2.85 reported by Davidson and Jameson[32] and demonstrates that $[PtBr_6]^{2-}$ is more stable than $[PtCl_6]^{2-}$ in aqueous solutions.

Speciation in Mixtures of H_2PtCl_6 and H_2PtBr_6. The spectrum of equimolar mixtures of H_2PtCl_6 and H_2PtBr_6 (with a $[Pt]_t$ of 0.48 M prepared in a 0.12 M $HClO_4$ solution to suppress hydrolysis), clearly shows the presence of all possible $[PtCl_{6-n}Br_n]^{2-}$ ($n = 0-6$) species, including possible geometric isomers (Figure 4a). ^{195}Pt chemical shifts observed for the nonaquated species $[PtCl_{6-n}Br_n]^{2-}$ species are almost identical to those reported by Von Zelewsky[19] and Kerrison.[38] In the spectra shown in Figure 4a, the observed relative ratios of the *cis*- to *trans*-$[PtCl_4Br_2]^{2-}$ and $[PtCl_2Br_4]^{2-}$ isomers (~4:1), as well as those of the *fac*- to *mer*-$[PtCl_3Br_3]^{2-}$ isomers (~2:3) are very close to those predicted on a statistical basis. Significantly in these spectra the newly identified $[PtBr_5(H_2O)]^-$ complex at −1004 ppm, as well as a very small amount of $[PtCl_5(H_2O)]^-$ at 510 ppm, can be seen (the latter species *not* shown in spectral window of Figure 4a).

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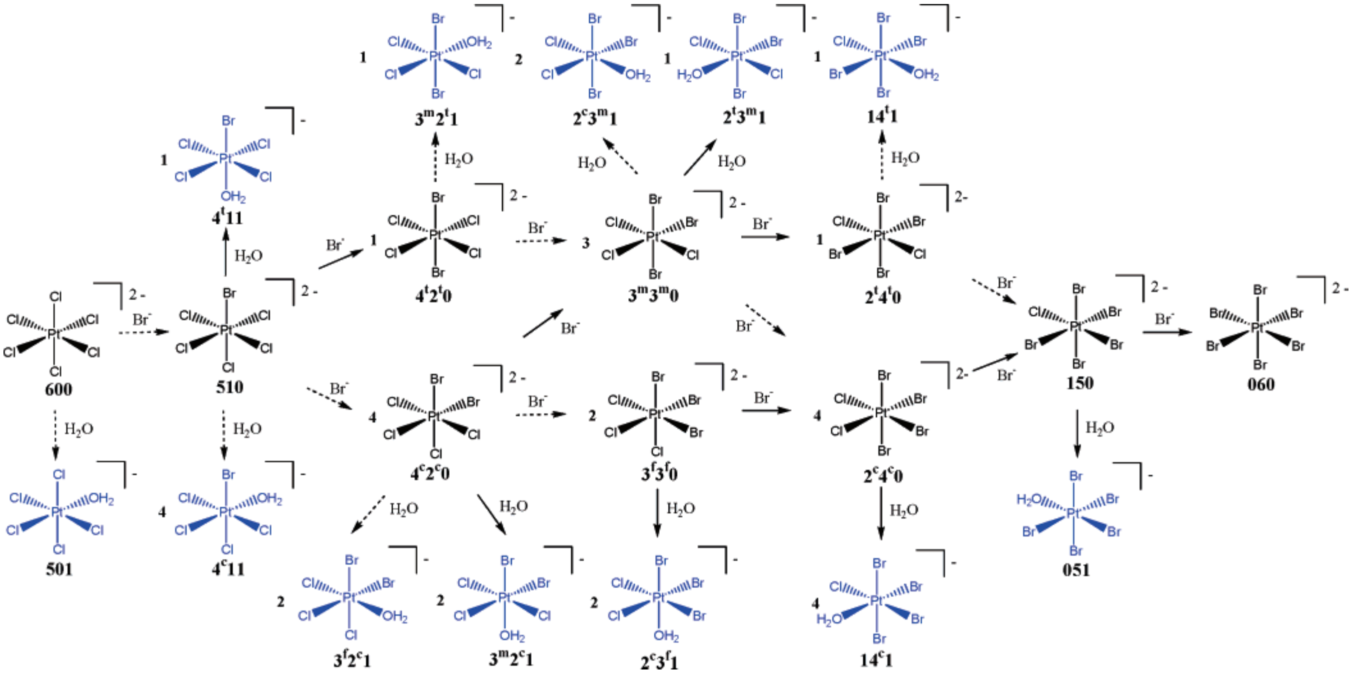
Scheme 1[a]



[a] Reaction scheme for the stepwise replacement in $[PtCl_6]^{2-}$ of chloride with bromide, as well as for the formation of $[PtCl_{5-n}Br_n(H_2O)]^-$ species (marked blue, $n = 0-5$). The designation of species has been adapted from Drews and Preetz.[40] The bold numbers to the left of the species represent the statistically expected isomeric ratio when applicable. Full arrows represent substitutions of Cl^- by either Br^- or H_2O at a position trans to a Br^- ion. Substitutions at a position trans to a Cl^- ion are represented by a dashed arrow (*not* all possible substitution pathways are shown in the interest of clarity, see text).

In these mixed-halide solutions, a number of other ^{195}Pt resonances not previously reported can be seen, the assignment of which are based on the generally systematic chemical shift trends obtained under steady state conditions in solution, are shown in Figure 4b. Generally an increase in the relative integrated intensity of all these previously unobserved resonances relative to the well-established $[PtCl_{6}-nBr_n]^{2-}$ signals is seen upon dilution of the sample, suggesting that these signals are from aquated complexes. Moreover, the statistically expected geometric isomeric isomer distribution, as determined from the integral ratios of the $[PtCl_{6-n}Br_n]^{2-}$ species, may be used to distinguish between the isomers of their aquated counterparts, taking into account the expected differences in trans influence of the Cl^- ion compared to the Br^- ion.[39] As noted above, aquation of $[PtBr_6]^{2-}$ to give $[PtBr_5(H_2O)]^-$ occurs to a lesser extent compared to that of $[PtCl_6]^{2-}$, and thus Cl^- substitution by H_2O is expected to predominate over that of Br^- by H_2O in these mixed halide solutions. The low pH (<2) of these solutions precludes hydrolysis of coordinated water, ruling out the presence of significant amounts of hydroxo complex species. These factors support the assignment of these minor resonances to *monoaqua* species of general formula $[PtCl_{5-n}Br_n(H_2O)]^-$ ($n = 0-5$) in Figure 4, since any *diaqua* complexes in this study have not been detected under any conditions. Significantly these ^{195}Pt assignments are confirmed by the more detailed graphical trend analysis of chemical shifts as discussed below.

^{195}Pt Chemical Shift Trend Analysis as a Method of Assignments of $[PtCl_{5-n}Br_n(H_2O)]^-$ Species. The octahedral representation of all the possible twelve $[PtCl_{5-n}Br_n(H_2O)]^-$ complexes ($n = 0-5$) is shown in Scheme 1, resulting from the stepwise substitution of Cl^- by Br^- in $[PtCl_6]^{2-}$, as well as for the aquation of the mixed halide complexes $[PtCl_{6-n}Br_n]^{2-}$ ($n = 0-6$). Each complex species is assigned a unique identification code based on the nomenclature adapted from Drews and Preetz.[40] The first numeral in this code represents the number of chloride ions in the octahedral complex; the second numeral signifies the number of bromide ions, while the third numeral indicates the number of water molecules coordinated to the Pt(IV) ion (in this case either 0 or 1). The configuration of possible geometric isomers is given as a superscript (c for cis, t for trans, m for meridional, and f for facial); the bold number to the left of the species represents the statistically expected relative ratio of possible geometric isomers. Solid arrows indicate substitutions of Cl^- by either Br^- or H_2O at a position trans to a Br^- ion, which are favored over the corresponding substitutions trans to a Cl^- ion (represented by a dashed arrow) in view of the relatively stronger trans effect of the Br^- ion.[39,41,42] (Other possible direct conversions between species (e.g., 501 → 411 → 321, etc.) are omitted in Scheme 1 for clarity)

In our ^{195}Pt spectra, all 12 $[PtCl_{5-n}Br_n(H_2O)]^-$ species could be observed (Figure 4b) and assigned as shown in Table 1. Because of the slight preference of Br^- over Cl^-

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Table 1. ^{195}Pt Chemical Shifts of $[PtCl_{6-n}Br_n]^{2-}$ ($n = 0-6$) and $[PtCl_{5-n}Br_n(H_2O)]^-$ ($n = 0-5$) Species, the Chemical Shift Differences, and Relative Concentrations of Species in an Equimolar Solution of $H_2PtCl_6{\cdot}H_2O$ and H_2PtBr_6 (0.48 M) in 0.12 M $HClO_4$

$[PtCl_{5-n}Br_n(H_2O)]^-$ species[a]	δ^{195}Pt (ppm)	predicted relative amount[b]	observed relative amount[b]	$[PtCl_{6-n}Br_n]^{2-}$ species[a]	δ^{195}Pt (ppm)	$\Delta^2(\delta^{195}Pt)$ (ppm)[c]
501	+510	1	1	**600**	+8	502
$4^{c}11$	+235	4	3	**510**	−278	513
$4^{t}11$	+207	1	1	**510**	−278	485
$3^{f}2^{c}1$	−50	2	2	**$4^{c}2^{c}0$**	−575	525
$3^{m}2^{t}1$	−53	1	1	**$4^{t}2^{t}0$**	−577	524
$3^{m}2^{c}1$	−78	2	3	**$4^{c}2^{c}0$**	−575	497
$2^{c}3^{m}1$	−349	2	1	**$3^{m}3^{m}0$**	−885	536
$2^{c}3^{f}1$	−373	2	2	**$3^{f}3^{f}0$**	−883	510
$2^{t}3^{m}1$	−377	1	1	**$3^{m}3^{m}0$**	−885	508
$14^{t}1$	−658	1	1	**$2^{t}4^{t}0$**	−1207	549
$14^{c}1$	−683	4	10	**$2^{c}4^{c}0$**	−1204	521
051	−1004	1	1	**150**	−1538	534

[a] Nomenclature for species has been adapted from Drews and Preetz.[40] [b] The statistically predicted lowest amount was set to 1. [c] Chemical shift difference $\Delta^2(\delta^{195}Pt)$ between the $[PtCl_{6-n}Br_n]^{2-}$ species and the corresponding $[PtCl_{5-n}Br_n(H_2O)]^-$ species.

to coordinate to Pt(IV), the steady-state concentration of $[PtCl_6]^{2-}$ is relatively low in mixtures derived from equimolar amounts of H_2PtCl_6 and H_2PtBr_6 so that the ^{195}Pt signal of $[PtCl_5(H_2O)]^-$ is only just detectable at 510 ppm. With reference to Scheme 1 and proceeding with aquation from left to right, this results in two signals corresponding to isomers of the $[PtCl_4Br(H_2O)]^-$ complex. Taking into account the statistically expected amounts (on the basis of the relatively higher trans effect of Br^-), we assigned the two species at 235 and 207 ppm to **$4^{c}11$** and **$4^{t}11$**, respectively. Evidently, the **$4^{c}11$** species with a water molecule positioned trans to a Cl^- ion experiences a more downfield shift of 28 ppm than the complex **$4^{t}11$** with a water molecule positioned trans to a Br^- ion. Additional support for the assignment of $[PtCl_4Br(H_2O)]^-$ isomers is derived from an average difference, $\Delta(\delta^{195}Pt)$, of 499 ppm between these species and the corresponding nonaquated complexes $[PtCl_5Br]^{2-}$, corresponding well to substitution one Cl^- ion by H_2O in the chloro series of complexes. In a similar fashion, the three nonequivalent isomers of $[PtCl_3Br_2(H_2O)]^-$ can be assigned to the resonances at −50, −53, and −78 ppm; since the average $\Delta(\delta^{195}Pt)$ between the two close-lying peaks found at −50 and −53 ppm and the upfield signal (at −78 ppm) is 27 ppm is virtually identical to that observed between the two previously assigned $[PtCl_4Br(H_2O)]^-$ isomers, the following general conclusion can be thus made: *substitution of Cl^- by H_2O at a position trans to a Cl^- ion causes a larger $\Delta(\delta^{195}Pt)$ than substitution of Cl^- by H_2O at a position trans to a Br^- ion*. This general trend provides an empirical means for the correct isomeric assignments in such cases, so that the $[PtCl_{5-n}Br_n(H_2O)]^-$ isomers with a water molecule positioned trans to a Cl^- ion should experience downfield shifts some 25−30 ppm larger than those complexes in which a water molecule is trans to a Br^- ion. Consequently, the two more downfield peaks of the three $[PtCl_3Br_2(H_2O)]^-$ isomers can be assigned to **$3^{f}2^{c}1$** (at −50 ppm) and **$3^{m}2^{t}1$** (at −53 ppm), while the signal at −78 belongs to **$3^{m}2^{c}1$**. The reverse pattern is observed for the three $[PtCl_2Br_3(H_2O)]^-$ isomers with the more downfield peak at −349 ppm corresponding to the **$2^{c}3^{m}1$** species, while the other two close-lying isomers, **$2^{c}3^{f}1$** and **$2^{t}3^{m}1$**, have δ^{195}Pt peaks ~27 ppm upfield at −373 and −377 ppm, respectively. The relatively intense resonance at −683 ppm corresponds to the cis isomer **$14^{c}1$**, which is 521 ppm downfield relative to *cis*-$[PtCl_2Br_4]^{2-}$; in contrast, the trans isomer **$14^{t}1$** is only just observable at 25 ppm downfield from **$14^{c}1$**. The most upfield peak at $\delta^{195}Pt = -1004$ ppm is assigned to the aquated **051** species $[PtBr_5(H_2O)]^-$ (cf previous section). It should be noted that the relative concentrations of the possible geometric isomers of the $[PtCl_{5-n}Br_n(H_2O)]^-$ species differ in some cases considerably from those statistically expected (Table 1), something most pronounced for the $[PtClBr_4(H_2O)]^-$ isomers, which is most probably the consequence of the

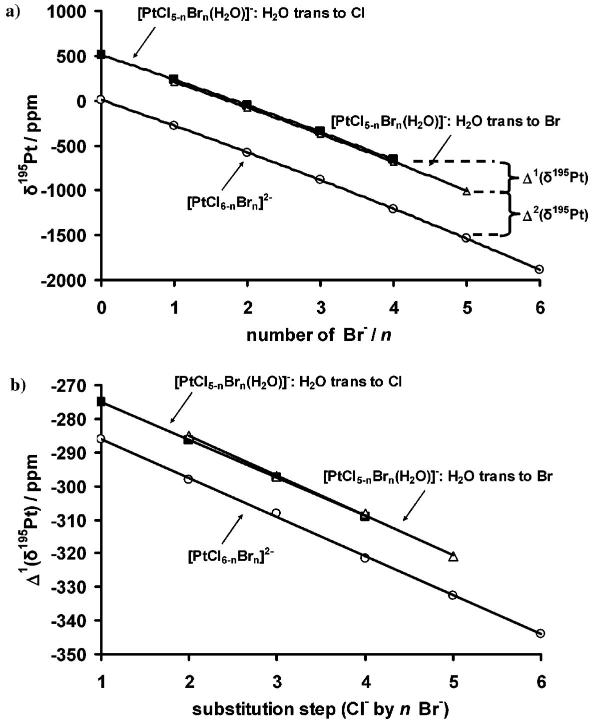

Figure 5. (a) ^{195}Pt chemical shifts of $[PtCl_{6-n}Br_n]^{2-}$ (○, $n = 0-6$) and $[PtCl_{5-n}Br_n(H_2O)]^-$ species where Cl^- is substituted by H_2O at a position trans to Cl^- (■, $n = 0-4$) or at a position trans to Br^- (△, $n = 1-5$) in a solution of $H_2PtCl_6{\cdot}H_2O$ and H_2PtBr_6 in 0.12 M $HClO_4$ (total Pt concentration is 0.48 M). (**b**) Chemical shift increments $\Delta(\delta^{195}Pt)$, between the $[PtCl_{6-n}Br_n]^{2-}$ species ($\Delta^{1A}(\delta^{195}Pt)$, ○) and between the $[PtCl_{5-n}Br_n(H_2O)]^-$ species for the substitution of Cl^- by H_2O at a position trans to Cl^- ($\Delta^{1B}(\delta^{195}Pt)$, ■) or at a position trans to Br^- ($\Delta^{1C}(\delta^{195}Pt)$, △).

relatively higher trans effect of the Br^- ion compared to the Cl^- ion, as implied by the solid and dashed arrows in Scheme 1.

A detailed trend analysis of the ^{195}Pt NMR chemical shifts in this study shows that substitution of Cl^- by Br^- in $[PtCl_6]^{2-}$ results in a monotonic increase in the shielding of the ^{195}Pt nucleus as a function of the number of Br atoms in the complex, although this trend is not perfectly linear; plots of δ^{195}Pt for both the series of $[PtCl_{6-n}Br_n]^{2-}$ species and their corresponding aquated $[PtCl_{5-n}Br_n(H_2O)]^-$ equivalents as a function n, the number of bromide ions, reveal parallel *second-order* relationships ($R^2 = 1.0000$) for these two sets of complexes, as shown in Figure 5a. These relationships can be represented by $\delta^{195}\text{Pt} = 7.9 - 280.0n - 5.8n^2$ (eq 5a, $n = 1-6$) for the $[PtCl_{6-n}Br_n]^{2-}$ series of complexes, $\delta^{195}\text{Pt} = 509.9 - 268.6n - 5.9n^2$ (eq 5b, $n = 0-4$) for the $[PtCl_{5-n}Br_n(H_2O)]^-$ complexes, in which a H_2O molecule has replaced a Cl^- ion trans to a coordinated chloride ion, and $\delta^{195}\text{Pt} = 478.4 - 265.4n - 6.2n^2$ (eq 5c, $n = 1-5$) for the $[PtCl_{5-n}Br_n(H_2O)]^-$ complexes, in which a H_2O molecule has replaced a Cl^- ion trans to a coordinated bromide ion. The first derivative of these trend lines (or chemical shift increments, hereafter $\Delta^1(\delta^{195}\text{Pt})$, Figure 5b) display a linear relationship as a function of n: $\Delta^{1A}(\delta^{195}\text{Pt}) = -274.3 - 11.6n$ (eq 6a, $R^2 = 0.9991$) for the $[PtCl_{6-n}Br_n]^{2-}$ series of complexes. This implies that each Cl^- substitution by a Br^- ion induces a ∼286 upfield shift in δ^{195}Pt, but for each Br^- already within the coordination sphere, an additional ∼12 ppm upfield shift occurs. Likewise, the chemical shift increments for the series of complexes of $[PtCl_{5-n}Br_n(H_2O)]^-$ in which a H_2O molecule substitutes a Cl^- ion trans to a coordinated chloride ion, results in the virtually perfect linear trend $\Delta^{1B}(\delta^{195}\text{Pt}) = -263.8 - 11.3n$ (eq 6b, $n = 1-4$, $R^2 = 0.9999$). Similarly, substitution of a Cl^- by a H_2O molecule trans to a bromide ion gives a relationship $\Delta^{1C}(\delta^{195}\text{Pt}) = -261.1 - 11.9n$ (eq 6c, $n = 2-5$, $R^2=0.9990$), as shown in Figure 5b.

The differences in δ^{195}Pt between $[PtCl_{5-n}Br_n(H_2O)]^-$ and their corresponding $[PtCl_{6-n}Br_n]^{2-}$ equivalents listed in Table 1, $\Delta^2(\delta^{195}\text{Pt})$, again show linear trends with n resulting in $\Delta^{2A}(\delta^{195}\text{Pt}) = 501.5 + 11.7n$ (eq 7a, where $n = 0-4$, $R^2=0.9991$) for substitution of a Cl^- trans to a bound chloride ion by a H_2O molecule and $\Delta^{2B}(\delta^{195}\text{Pt}) = 472.6 + 12.2n$ (eq 7b, $n = 1-5$, $R^2 = 0.9997$) for the corresponding substitution trans to a coordinated bromide ion. An additional (upfield) shift contribution of 12 ppm for each Br^- already present is observed, as expected. A similar regular pattern for chemical shift increments for halide substitution has been previously reported (also reported for non-Pt complexes): Kidd and Truax,[43] for example reported on a monotonic, nonlinear downfield shift in δ^{27}Al on substitution of Cl^- by Br^- or I^- in $AlCl_4^-$, whereas Kerrison reported incremental δ^{195}Pt trends for Pt(II/IV) nitro-chloro-bromo complexes.[42] These trends are clearly related to the differences induced in the various shielding contributions making up the total shielding of the ^{195}Pt nucleus in these complexes.

Although the detailed theoretical interpretation of the above-mentioned empirical chemical shift trends is beyond the scope of this paper, some comment is appropriate. The complexity of factors which account for the actual ^{195}Pt chemical shifts for even "simple" Pt(IV) and Pt(II) complexes, has been demonstrated inter alia by a density functional (DFT) computational study by Ziegler,[44] and confirmed by Autschbach.[45] These authors emphasize the importance of incorporating spin−orbit coupling and relativistic effects for accurately accounting of ^{195}Pt chemical shifts, in addition to the paramagnetic shielding contribution rationalized by the generally used, but insufficient, Ramsey model of nuclear shielding of heavy nuclei such as δ^{195}Pt.[16,46,47,48] Recent theoretical work by Penka Fowe et al,[49] who used DFT calculations to calculate the ^{195}Pt chemical shifts of the $[PtCl_{6-n}Br_n]^{2-}$ complexes, have confirmed this, while Sterzel and Autschbach highlighted the influence of unspecific solvent effects and structural parameters in accurately calculating ^{195}Pt chemical shifts.[50] We are also currently undertaking computational work to elucidate the nature of trends in the δ^{195}Pt chemical shifts of the series of $[PtCl_{6-n}Br_n]^{2-}$, $[PtCl_{5-n}Br_n(H_2O)]^-$, and related Pt(IV) complexes, preliminary results of which have recently been published.[51]

Nature of Pt(IV) Complexes Extracted by Diethylenetriamine-Modified Silica-Based Anion Exchangers from $\mathbf{H_2PtCl_6}$ Solutions. The yellow/brown 0.48 M aqueous solution of H_2PtCl_6 was contacted with fresh 100 mg portions of ion exchanger **1**, such that sufficient solution remained after extraction, and the total extractive capacity of the 100 mg portion of **1** (∼93 μmol of the diethylenetriamine moiety, see the Experimental Section) was significantly less that the total amount of H_2PtCl_6 present in solution. After 60 s of contact time, the supernatant was rapidly separated from the "loaded" **1,** and a ^{195}Pt NMR spectrum of the solution was recorded within 5 min, which showed only two peaks of $[PtCl_6]^{2-}$ and the $[PtCl_5(H_2O)]^-$ complex (apart from the external reference peak). This contact time was found to be sufficient, since rapid extraction occurred as shown by the immediate color change of **1** from white to yellow/brown. A series of ^{195}Pt NMR spectra from solutions before and after each of six additions of a fresh portion of **1** are shown

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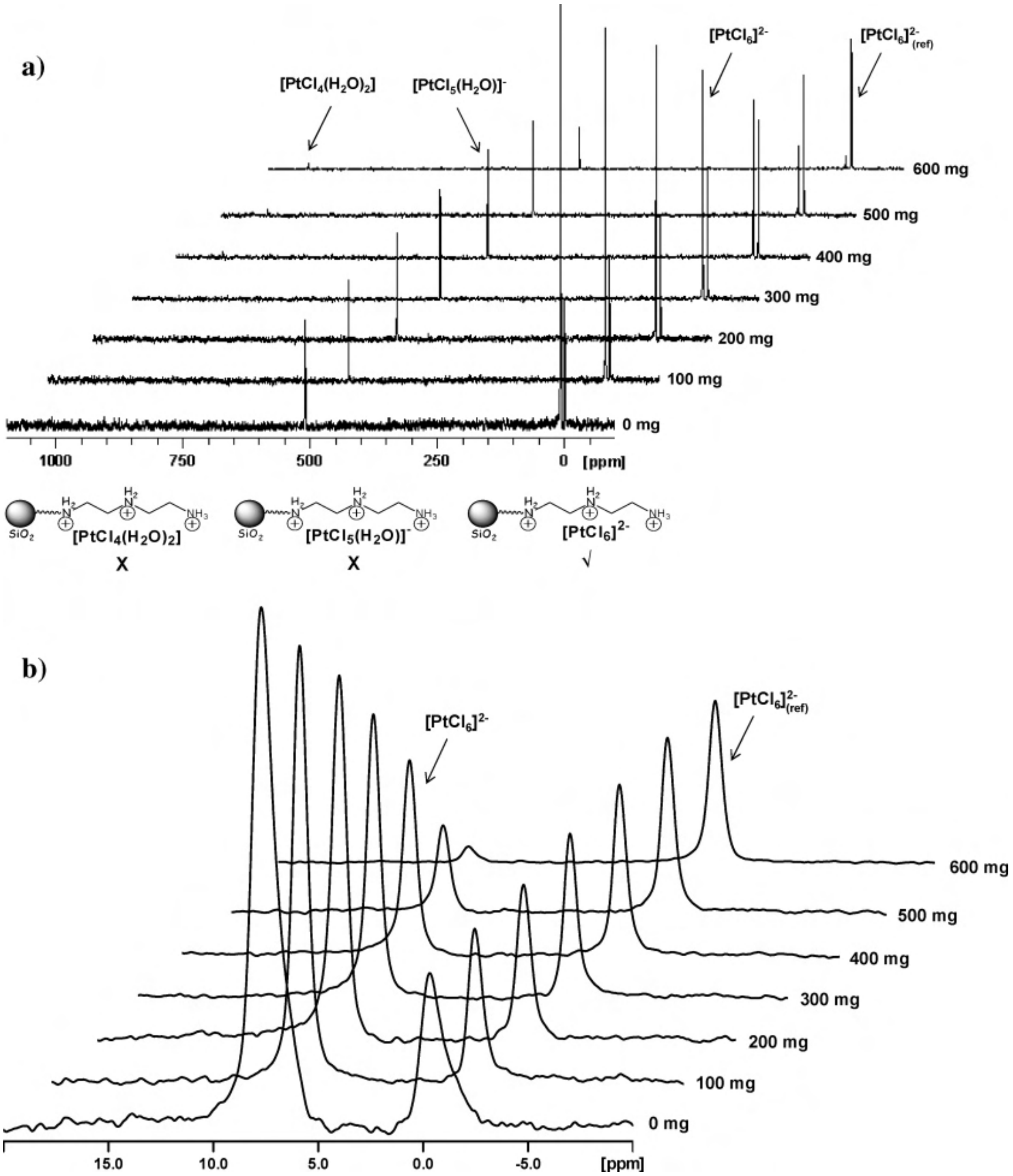

Figure 6. ^{195}Pt NMR spectra of (a) an aqueous solution (initial $[Pt]_t = 0.48$ M) of H_2PtCl_6 before and after consecutive extractions using 100 mg of fresh ion exchanger **1** and (b) a detailed view of the $[PtCl_6]^{2-}$signals of the spectra.

in Figure 6a, showing extraction of $[PtCl_6]^{2-}$ by the steady decrease of the peak intensity of $[PtCl_6]^{2-}$ upon each addition of fresh **1** (Figure 6b). By contrast, the intensity of the $[PtCl_5(H_2O)]^-$ signal remained virtually unaffected until the last extraction, indicating *preferential* extraction of $[PtCl_6]^{2-}$ over $[PtCl_5(H_2O)]^-$.

To verify that in each of the solutions after extraction the distribution of the species had reached a steady-state, ^{195}Pt NMR spectra were re-recorded several times (within ~1 h) before the next extraction was performed showing that no significant intensity changes occurred over the time scale of measuring the ^{195}Pt NMR spectra, confirming that no anation or aquation redistribution of the equilibria of eq 2 takes place. This was also confirmed by the invariance of ^{195}Pt NMR spectra acquired for some solutions over a period of months in separate, repeat experiments.

The relative integrated intensity of the peak from $[PtCl_5(H_2O)]^-$ gradually increases from some 18% prior to the first extraction, to almost 70% after the sixth addition of **1**. After the fifth extraction, for which there is a higher concentration of $[PtCl_5(H_2O)]^-$ in solution than that of $[PtCl_6]^{2-}$, preferential extraction of the latter species apparently still occurs; only after the sixth addition of **1**, when the solution is virtually depleted of platinum complexes, a point is reached where $[PtCl_5(H_2O)]^-$ is extracted as shown by the disappearance of this peak. A plot of the ratio of the peak areas of $[PtCl_6]^{2-}/[PtCl_6]^{2-}_{ref}$ and $[PtCl_5(H_2O)]^-/[PtCl_6]^{2-}_{ref}$ confirms preferential extraction of $[PtCl_6]^{2-}$ since the ratio of $[PtCl_6]^{2-}/[PtCl_6]^{2-}_{ref}$ gradually decreases after each addition of **1**, while the ratio of $[PtCl_5(H_2O)]^-/[PtCl_6]^{2-}_{ref}$ remains unaffected until the last two additions, after which the solution becomes virtually depleted of

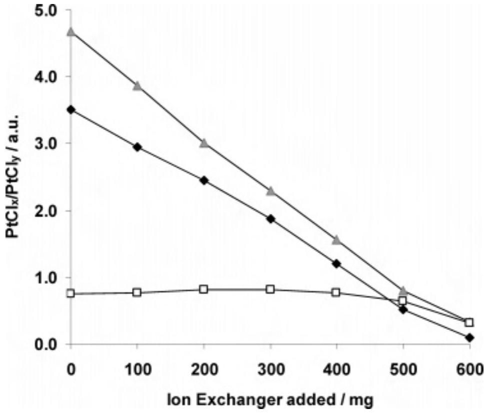

Figure 7. Relative ratio (in arbitrary units) of integrated peak areas of $[PtCl_6]^{2-}$ (♦), and $[PtCl_5(H_2O)]^-$ (□) relative to the $[PtCl_6]^{2-}{}_{ref}$ (insert) and of $[PtCl_6]^{2-}$ relative to $[PtCl_5(H_2O)]^-$ (gray triangle) before and after consecutive additions of 100 mg portions of fresh **1** to H_2PtCl_6 in water, (initial $[Pt]_t = 0.48$ M).

dissolved Pt(IV) species, showing that finally even the $[PtCl_5(H_2O)]^-$ complex is extracted from solution (Figure 7).

An interesting finding from the ^{195}Pt NMR spectra of solutions of H_2PtCl_6 after contact with the first three portions of **1** in this context, is that a small additional ^{195}Pt peak at 1009 ppm, attributable to $[PtCl_4(H_2O)_2]$, becomes apparent. The latter complex is not extracted even after the addition of the last portion of **1** suggesting that successive contact periods with **1** leads to the removal of $[PtCl_6]^{2-}$ and $[PtCl_5(H_2O)]^-$, so that the overall decrease in $[Pt]_t$ results in an increased degree of aquation of $[PtCl_6]^{2-}$ and $[PtCl_5(H_2O)]^-$, consistent with the concentration dependence of the aquation of H_2PtCl_6 data in Figure 2. On the other hand, upon extraction of $[PtCl_6]^{2-}$ from solution, this species may be expected to be replenished by Cl^- anation of $[PtCl_5(H_2O)]^-$, provided sufficient unbound Cl^- ions are available in solution (presumably liberated by aquation of $[PtCl_6]^{2-}$). Since upon addition of **1,** protonation of the poly(amine) is likely to occur, it is not unreasonable to expect some concomitant unbound Cl^- ion extraction from solution, so inhibiting anation. This hypothesis could be verified by the addition of a small quantity of NaCl (corresponding to about half of the amount of unbound Cl^- ions estimated to be present in a solution *before* extraction), to a 0.2 M H_2PtCl_6 solution which had been contacted with 100 mg of **1**. Addition of NaCl results in the initial concentration ratio $[PtCl_5(H_2O)]^-/[PtCl_6]^{2-}$ of 0.82 to rapidly dropping to 0.54, confirming that additional Cl^- in solution results in the expected redistribution of the equilibrium in eq 2. The observed order of Pt(IV) anion extraction is $[PtCl_6]^{2-} > [PtCl_5(H_2O)]^- \gg [PtCl_4(H_2O)_2]$, which follows the anticipated tendency of dinegatively charged $[PtCl_6]^{2-}$ anions to form ion-pairs with anion exchangers more readily than aquated species.[2] Apart from the decrease in net charge of these aquated species, it is not unreasonable to expect $[PtCl_5(H_2O)]^-$ and $[PtCl_4(H_2O)_2]$ to be relatively more hydrophilic in view of the hydrogen-bonding capability of these aquated platinum complexes, so favoring the aqueous phase. Our findings are consistent with a solvent extraction study in which $[PtCl_6]^{2-}$ or $[PtBr_6]^{2-}$ were the only species found to be extracted from aqueous solutions of H_2PtX_6 (X = Cl, Br) solutions into CCl_4 or cyclohexane with an amine-containing extractant, as monitored by spectrophotometric methods.[15]

Preferential $[PtBr_6]^{2-}/[PtCl_{6-n}Br_n]^{2-}$ Extraction from Aqueous H_2PtBr_6 and Mixtures of H_2PtCl_6 and H_2PtBr_6. Figure 8 shows the results of successive additions of **1** to a

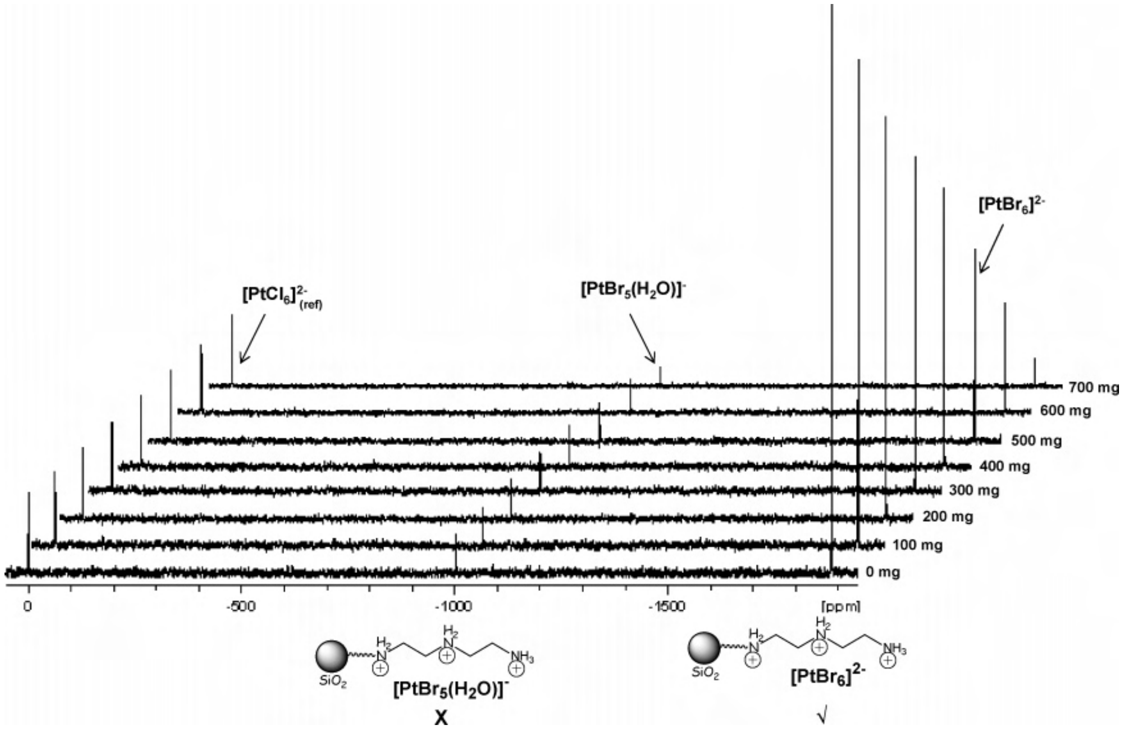

Figure 8. ^{195}Pt NMR spectra of an aqueous solution (initial $[Pt]_t = 0.48$ M) of H_2PtBr_6 before and after consecutive extractions with 100 mg portions of **1**.

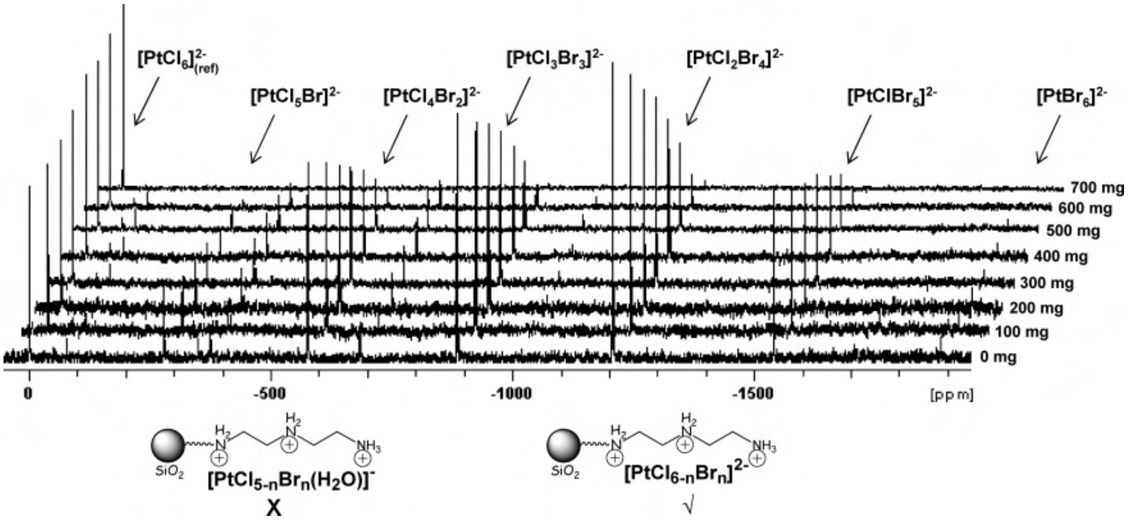

Figure 9. ^{195}Pt NMR spectra of an equimolar mixture (initial total Pt concentration is 0.48 M) of H_2PtCl_6 and H_2PtBr_6 in a 0.12 M $HClO_4$ solution before and after consecutive extractions using fresh 100 mg of ion exchanger **1**.

bright red aqueous solution of 0.48 M H_2PtBr_6. As for the H_2PtCl_6 solution, very rapid extraction was observed, shown by the white color of **1** turning deep-red within 60 s of contact time. The selective extraction behavior is almost identical to that observed for the H_2PtCl_6 solutions: $[PtBr_6]^{2-}$ is efficiently immobilized from solution upon each new addition of **1**, whereas the relative concentration of $[PtBr_5(H_2O)]^-$ remains unchanged, being only extracted to some extent upon the last addition of **1** (700 mg), resulting in roughly the same relative residual concentrations of $[PtBr_6]^{2-}$ and $[PtBr_5(H_2O)]^-$ in solution; the addition of an excess of **1** results in the final removal of both anionic species.

To establish possible differences in extractability of the series of mixed $[PtCl_{6-n}Br_n]^{2-}$ complexes and their corresponding aquated counterparts, an equimolar mixture of H_2PtCl_6 and H_2PtBr_6 was put into contact with fresh 100 mg batches of **1**. Figure 9 shows the ^{195}Pt NMR spectra before and after successive additions of **1** to the orange-colored aqueous solution (where $[Pt]_t$ is 0.48 M) of the mixture, whereby the color of the **1** changed from off-white into bright orange, indicative of binding of the *mixed* Pt halides. A gradual decrease of all the $[PtCl_{6-n}Br_n]^{2-}$ signals is observed with increased contact of the solution with fresh portions of **1**. Comparison of the relative intensities of the various signals of nonaquated complexes after each extraction indicated that no preferential extraction of any of the different $[PtCl_{6-n}Br_n]^{2-}$ species can be detected by this ^{195}Pt NMR method. As observed for the H_2PtCl_6 and H_2PtBr_6 systems above, the aquated mixed-halide complexes are only removed from solution after the last addition of **1,** after which virtually all the $[PtCl_6{-}nBr_n]^{2-}$ species were absent from solution. The consistency of trends for the single component H_2PtCl_6 and H_2PtBr_6, as well as the mixed-halide system, lends general support to the conclusion of preferential extraction of the $[PtX_6]^{2-}$ ($X = Cl^-$, Br^-) anions by anion exchange materials, such as **1** studied here, and underlines the importance of speciation in determining efficient and complete extraction of these anions.

Conclusions

^{195}Pt NMR is a powerful technique to study Pt speciation in aqueous solutions. A species distribution plot of the $[PtCl_6]^{2-}$, $[PtCl_5(H_2O)]^-$, and $[PtCl_4(H_2O)_2]$ shows that in equilibrated, relatively concentrated H_2PtCl_6 ($[Pt]_t > 0.12$ M) solutions in water the $[PtCl_4(H_2O)_2]$ is below the ^{195}Pt NMR detection limit, but for total $[Pt]_t$ concentrations of <0.1 M, the relative amounts of $[PtCl_5(H_2O)]^-$ and $[PtCl_4(H_2O)_2]$ species significantly increases, as a result of aquation reactions of the $[PtCl_6]^{2-}$ and $[PtCl_5(H_2O)]^-$ complexes under these conditions. From the analysis of the distribution of species data, the estimated $\log K_6 \approx 1.75 \pm 0.05$ (eq 2a) for the aquation of the $[PtCl_6]^{2-}$ in water and $\log K_6 \approx 2.7 \pm 0.15$ for the corresponding $[PtBr_6]^{2-}$ system in 0.12 M $HClO_4$ (eq 4) are in good agreement with literature data, which lends confidence to this technique. In mixtures of equimolar quantities of H_2PtCl_6/H_2PtBr_6 in water, a number of previously unidentified complexes of the general formula $[PtCl_{5-n}Br_n(H_2O)]^-$ ($n = 0-5$) could be clearly identified from their ^{195}Pt NMR spectra, and the assignments were confirmed by the remarkably linear relationships between the chemical shift increment, $\Delta(\delta^{195}\mathrm{Pt})$, of the aquated complexes as a function of the substitution of Cl^- ions by n Br^- ions, comparable to that established for the $[PtCl_{6-n}Br_n]^{2-}$ species. Moreover the possible geometric isomers of $[PtCl_3Br_2(H_2O)]^-$, $[PtCl_2Br_3(H_2O)]^-$, and $[PtCl_4Br(H_2O)]^-$ were identified on the basis of the finding that substitution of Cl^- by H_2O at a position *trans to a* Cl^- *ion* systematically causes a 25−30 ppm larger $\Delta(\delta^{195}\mathrm{Pt})$ than substitution of Cl^- by H_2O at a position *trans to a* Br^- *ion.*

^{195}Pt NMR is also useful for determining the nature and extent of the Pt(IV)chloro, Pt(IV)bromo, and mixed Pt(IV)-chloro-bromo complex anions extracted from acidic aqueous solutions by silica-based diethylenetriamine ion exchangers. For the solutions derived from H_2PtX_6 ($X = Cl^-$, Br^-, or a mixture of the two Pt(IV)salts), preferential extraction of the $[PtX_6]^{2-}$ anions over their corresponding aquated $[PtX_5(H_2O)]^-$ counterparts takes place initially. Although the ion exchanger has a preference for $[PtX_6]^{2-}$, some affinity for monoaquated platinum(IV) halide complexes has also been demonstrated in the presence of an excess of **1** relative to the total Pt(IV) complex concentration in solution.

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