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^{195}Pt NMR Chemical Shift Trend Analysis as a Method to Assign New Pt(IV)–Halohydroxo Complexes

Jurjen Kramer and Klaus R. Koch*

Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1,
Matieland, 7602 Stellenbosch, South Africa

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A ^{195}Pt NMR spectroscopy study of the speciation of $[PtCl_6]^{2-}$, $[PtBr_6]^{2-}$, and the mixed $[PtCl_{6-m}Br_m]^{2-}$ ($m = 0$–6) anions in aqueous medium after hydroxide ion substitution of coordinated halide ions has been carried out under dynamic conditions. Of the 56 possible $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ (m, $n = 0$–6) complex anions in solution under dynamic conditions, the relative chemical shifts $\delta(^{195}Pt)$ of 52 observable species have been assigned, 33 of which had not been reported previously. The assignment of all these species including the possible stereoisomers is facilitated by systematic *linear relationships* between the $\delta(^{195}Pt)$ *increments* resulting from substitutions of the halide ions by OH^- ions. Under dynamic conditions, the relative concentration (as indicated by resonance intensities) of the $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ (m, $n = 0$–6) species was found to be largely determined by the *trans* effects on ligand substitution reactions, leading to the transient appearance of previously unobserved complexes. Only the $\mathbf{2^c2^c2^t}$ and $\mathbf{2^t2^t2^t}$ isomers of the ternary $[PtCl_2Br_2(OH)_2]^{2-}$ complex, the $\mathbf{3^m12^t}$ $[PtCl_3Br(OH)_2]^{2-}$ and the $\mathbf{13^m2^t}$ $[PtClBr_3(OH)_2]^{2-}$ anions could not be observed under our conditions, although their $\delta(^{195}Pt)$ are confidently predictable from the linear trend analysis. This chemical shift trend analysis constitutes a powerful method for the virtually unambiguous assignment of ^{195}Pt chemical shifts for such complex anions undergoing slow ligand exchange on the NMR time scale, as facilitated by the strikingly good correlations of $\delta(^{195}Pt)$ for the species as a function of the number of hydroxide ions in the coordination sphere.

Introduction

The separation and efficient recovery of the platinum group metals (PGMs; Pt, Pd, Rh, Ir, Ru, and Os) in acidic chloride-rich process solutions depends on the formation of stable anionic metal chloride complexes of the type $[MCl_x]^{n-x}$, where M is the PGM ion, n its oxidation state (≤ 4) [this formula is not intended to include all possible PGM complex species, particularly, those for Ru and Os with higher (>4) oxidation states, and excludes the possibility of polynuclear complexes, which are not generally observed in the acidic chloride-rich solutions considered here], and x the number of coordinated Cl^- ions, typically 4 or 6, depending on the specific element.[1,2] Modern separation and recovery processes essentially require the selective transfer of such anionic chloro-complex species (e.g., $[PdCl_4]^{2-}$ and $[PtCl_6]^{2-}$ anions in the case of Pd(II) and Pt(IV), respectively) from an aqueous to a nonaqueous (organic) receptor phase.[3] In such process solutions, many factors such as the acidity, temperature, chloride and precious metal ion concentration, and the "age" of the solutions (which as a result of relative kinetic inertness to substitution is characteristic of these metal ions) largely determine the distribution of "species" of the complex anions which may occur as a result of the aquation or hydrolysis reactions of the $[MCl_x]^{n-x}$ complexes. Particularly for platinum(IV), the resulting $[PtCl_{x-y}(H_2O)_y]^{n-x+y}$ and $[PtCl_{x-z}(OH)_z]^{n-x}$ species (with $n = 2$ or 4; $x = 4$ or 6; y, $z = 0-6$) are generally less readily extracted.[2,3] The relatively high NMR receptivity of the ^{195}Pt isotope, the large chemical shift range ($\delta^{195}Pt > 13\,000$ ppm),[4] and the extreme sensitivity of $\delta(^{195}Pt)$ to the structure, geometrical isomers, oxidation state, and nature of the coordinated ligands of the

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* To whom correspondence should be addressed. E-mail: krk@sun.ac.za. Fax: +27 21 8083342. Phone: +27 21 8083020.

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Pt(II/IV) containing the molecular species under study[5,6] makes ^{195}Pt NMR spectroscopy a powerful method with which to study the "speciation" of these complexes in solutions comparable to industrial process streams.

We have recently shown ^{195}Pt NMR spectroscopy to be an excellent tool in a speciation and preferential extraction study of $[PtX_6]^{2-}$ species (X = Cl, Br, or a mixture of the two halides) over their corresponding aquated $[PtX_5(H_2O)]^-$ counterparts from aqueous acidic solutions by silica-based diethylenetriamine anion exchangers.[7] These studies were performed under acidic conditions (pH <2), in which the only species observable are the $[PtX_6]^{2-}$ and $[PtX_5(H_2O)]^-$ complexes, and in very dilute solutions, also small amounts of $[PtCl_4(H_2O)_2]$. In view of the relatively low pK_a values of the $[PtCl_5(H_2O)]^-$ and $[PtBr_5(H_2O)]^-$ species at pK_a = 3.5−3.8 and pK_a = 4.4, respectively,[8] in solutions with higher pH, one might anticipate extensive hydrolysis or substitution reactions of halides by OH^- ions in $[PtX_6]^{2-}$ and $[PtX_5(H_2O)]^-$ complexes. A survey of the literature shows only one ^{195}Pt NMR spectroscopy study of the hydrolysis products of $[PtCl_6]^{2-}$ over two decades ago by Carr et al.,[6] in addition to a related ^{195}Pt NMR study involving the Pt(IV)nitrito−chloro−bromo series of complexes.[9] Another related study in this context is a ^{195}Pt NMR study of water exchange of *trans*-dichlorodiaquaplatinum(II) and oxidative addition of Cl_2 to the $[Pt(H_2O)_4]^{2+}$ complexes in perchloric acid medium.[10]

Empirical studies show that ^{195}Pt chemical shifts are extremely sensitive to the specific structure of the Pt(IV) containing complex anion, as well as to other factors such as small differences in concentration, temperature, pH, and solvent composition.[11,12] In this context, we therefore investigated [we reinvestigated the series of $[PtCl_{6-n}(OH)_n]^{2-}$ complexes studied by Carr et al. to obtain a consistent set of $\delta(^{195}Pt)$ data for the trend analysis presented in this study vide infra] the full series of $[PtCl_{6-n}(OH)_n]^{2-}$, $[PtBr_{6-n}(OH)_n]^{2-}$ ($n = 0-6$), and mixed halide $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ (m, $n = 0-6$) complex anions with the aim of establishing a rapid and reliable method with which to identify various complex species under dynamic but well-defined conditions in Pt(IV)-containing solutions. We here present a full 129 MHz ^{195}Pt NMR assignment of 33 previously unobserved species of the 56 possible $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ complex anions, including virtually all of the geometrical isomers. These assignments could be confirmed by the remarkably systematic δ^{195}Pt shielding trends observed upon substitution of halide ions by hydroxide ions in Pt(IV) complexes. Moreover, such correlations lead to the fairly accurate prediction of ^{195}Pt chemical shifts particularly for related, but previously unobserved, Pt species under specified conditions.

Experimental Section

Reagents. All reagents and solvents were purchased from commercial sources and were used without further purification unless stated otherwise. The platinum salts $H_2PtCl_6{\cdot}xH_2O$ ($x \approx 2$), H_2PtBr_6 (Johnson Matthey PLC, Precious Metals Division), and $Na_2[Pt(OH)_6]$ (Aldrich) 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) and degassed by bubbling Ar gas through for at least 2 h prior to use. All aqueous NaOH additions were performed under Schlenk conditions and all solutions were stored likewise.

All solutions were prepared in subdued ambient light, in view of the possibility of photochemically induced effects as described previously.[7]

^{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 (δ^{195}Pt = 0.0 ppm) (500 mg cm^{-3} $H_2PtCl_6{\cdot}xH_2O$ ($x \approx 2$) 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 1500−2000 ppm. Spectra were recorded with a 2.0 μs excitation pulse (corresponding to a ~20° pulse) at maximum practical power and an acquisition time of 1.0 s with no relaxation delay, in an attempt to ensure homogeneous and complete excitation over the large spectral width; T_1 relaxation times of most of the platinum complexes were measured to be <150 ms in these solutions, which ensured essentially complete relaxation of all complex species in solution. A line-broadening factor of 20 Hz was applied resulting in an effective line-width at half-height for different resonances ranging from 40 to 80 Hz; the estimated accuracy of the measured δ^{195}Pt values is ±1 ppm. Under these conditions, the expected $^{35}Cl/^{37}Cl$ and $^{79}Br/^{81}Br$ isotope shifts were not resolved for most ^{195}Pt NMR peaks, but if desired, these can be observed under conditions of higher resolution. Given the very large spectral widths used to record the ^{195}Pt spectra in this work, it is not possible to achieve completely homogeneous excitation over the entire spectral width, with the consequence that the relative integral intensities of resonances, particularly the chemical shifts far from the transmitter offset at the center of the spectrum, may not accurately reflect the true concentration of the species in question. Nevertheless, under the conditions used here, an approximate correlation between peak intensity and relative concentration of a particular complex species may be reasonably expected (we thank one of the referees for drawing attention to this point). Hence no completely quantitive peak intensity information is implied (see below) in this study.

Hydroxide Ion Substitution Experiments. To observe all the $[PtCl_{6-n}(OH)_n]^{2-}$ species ($n = 0-6$) under one set of experimental conditions, 128 μL of a 5.0 M NaOH solution (3.2 molar equiv of OH^- ions to total Pt(IV) ions) was added to a solution (400 μL) of $H_2PtCl_6{\cdot}xH_2O$ ($x \approx 2$) in water (initial Pt concentration ($[Pt]_i$) is 0.5 M). To this solution, with a final Pt concentration ($[Pt]_f$) of 0.38 M, 14 mg of $Na_2[Pt(OH)_6]$ (0.04 mmol) was added. All ten $[PtBr_{6-n}(OH)_n]^{2-}$ ($n = 0-6$) species were visible in a 0.5 M $[Pt]_f$

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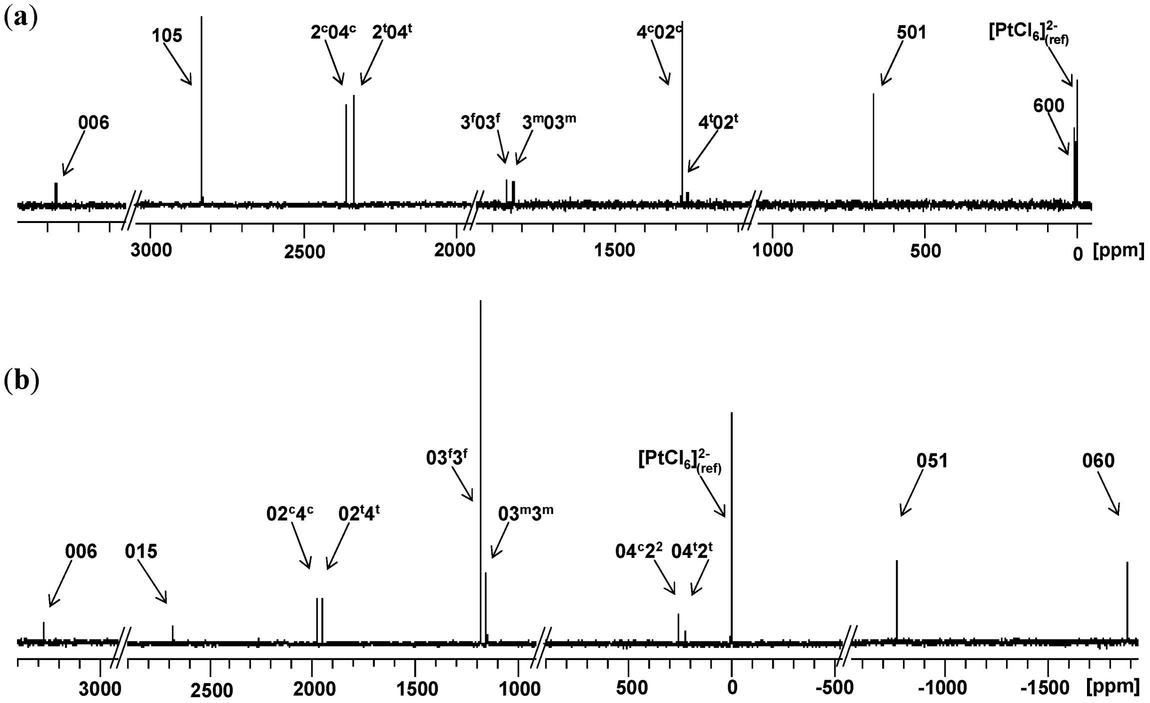

Figure 1. ^{195}Pt NMR spectra of **(a)** an aqueous solution of H_2PtCl_6 to which a total of 3.2 molar equiv of NaOH have been added ($[Pt]_f = 0.38$ M) and **(b)** an aqueous solution of H_2PtBr_6 with a total of 4.0 molar equiv of NaOH added ($[Pt]_f = 0.50$ M). The fully hydrolyzed $[Pt(OH)_6]^{2-}$ species (**006**) was observable only after addition of a small portion (~0.2 molar equiv to Pt) of $Na_2[Pt(OH)_6]^{2-}$ to these solutions. The nomenclature code for the species has been adapted from Drews and Preetz.[13]

solution (400 μL) of H_2PtBr_6 in 2.0 M NaOH (4.0 molar equiv of OH^- ions to total Pt(IV) ions), followed by the addition of 0.04 mmol $Na_2[Pt(OH)_6]$. To obtain the $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ (m, n = 0−6) complexes, an equimolar solution of $H_2PtCl_6{\cdot}xH_2O$ ($x \approx 2$) and H_2PtBr_6 ($[Pt]_i = 0.50$ M) in water was aged after mixing for at least 24 h to ensure that a steady-state had been reached, followed by addition of 2.1 molar equiv of NaOH (to total $[Pt]_f = 0.41$ M). The relative ^{195}Pt NMR peak intensities of the species present at very low concentrations in solution under these conditions could mostly be increased by changing the ratio of $H_2PtCl_6{\cdot}xH_2O$ ($x \approx 2$) to H_2PtBr_6 or by adding more NaOH solution.

The ^{195}Pt NMR spectra of the alkaline solutions were recorded deliberately under dynamic conditions before any steady-state had been reached because the objective was to observe as many of the complex species, including all stereoisomers, as possible. For this reason, the relative concentrations of the species as determined by the integrated peak areas are indicative of the *relative* concentrations of the complexes *at a fixed point in time* after the NaOH addition only and are not intended to convey any quantitative mechanistic information concerning the rate of formation or about the quantitative distribution of species.

Results and Discussion

^{195}Pt NMR Study of Hydroxide Ion Substitution in $[PtCl_6]^{2-}$ and $[PtBr_6]^{2-}$ Complexes. In the presence of a strong base, such as the OH^- ion (as NaOH), the hexachloroplatinate, $[PtCl_6]^{2-}$, complex may undergo substitution/hydrolysis [because it is not clear whether the hydroxyl species are formed by direct substitution of OH^- ions or via hydrolysis of the aquated species, the former term is used throughout the text without any mechanistic implication] reactions, forming $[PtCl_{6-n}(OH)_n]^{2-}$ (n = 1−6) complexes according to eq 1.

$$[PtCl_6]^{2-} + OH^- \rightleftharpoons [PtCl_5(OH)]^{2-} + Cl^- \quad (1a)$$

$$[PtCl_5(OH)]^{2-} + OH^- \rightleftharpoons (\mathit{cis,trans})[PtCl_4(OH)_2]^{2-} + Cl^- \quad (1b)$$

$$\vdots$$

$$[PtCl(OH)_5]^{2-} + OH^- \rightleftharpoons [Pt(OH)_6]^{2-} + Cl^- \quad (1f)$$

Evidently, the extent of OH^- substitution is dependent on the concentration of OH^- ions added (and possibly reaction time allowed). To obtain a sufficiently alkaline solution, in which essentially only OH^- substitution of choride could be observed, sodium hydroxide in excess of 2.0 molar equiv relative to hexachloroplatinic acid was required to neutralize the strong acid H_2PtCl_6. Thus upon addition of 3.2 molar equiv of a NaOH solution to a concentrated ($[Pt]_i = 0.50$ M) solution of H_2PtCl_6 (to pH ≈ 13), the initially bright yellow/brown solution immediately changed color to clear orange/brown, suggestive of fairly rapid ligand exchange. The ^{195}Pt NMR spectra of such solutions, acquired within 5−10 min after NaOH addition, confirmed that significant OH^- substitution had indeed taken place. In spectra recorded within ~2 h after the NaOH addition, all the $[PtCl_{6-n}(OH)_n]^{2-}$ (n = 0−5) complexes are observable, including all the possible stereoisomers, albeit some only as transient resonances (Figure 1a).

To facilitate the ^{195}Pt NMR assignment, each complex species is coded with a unique identification number based on the nomenclature adapted from Drews and Preetz.[13] The first numeral in this code represents the number of chloride

Table 1. ^{195}Pt Chemical Shift Assignments of All Observable $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ (m, $n = 0-6$) Complexes in an Alkaline Solution ($[Pt]_f = 0.38$ M)^{a}

$[PtCl_{6-n}(OH)_n]^{2-}$		$[PtCl_{5-n}Br(OH)_n]^{2-}$		$[PtCl_{4-n}Br_2(OH)_n]^{2-}$		$[PtCl_{3-n}Br_3(OH)_n]^{2-}$		$[PtCl_{2-n}Br_4(OH)_n]^{2-}$		$[PtCl_{1-n}Br_5(OH)_n]^{2-}$		$[PtBr_6]^{2-}$	
species^{b}	δ^{195}Pt^{c} (ppm)	species^{b}	δ^{195}Pt^{c} (ppm)	species^{b}	δ^{195}Pt^{c} (ppm)	species^{b}	δ^{195}Pt^{c} (ppm)	species^{b}	δ^{195}Pt^{c} (ppm)	species^{b}	δ^{195}Pt^{c} (ppm)	species^{b}	δ^{195}Pt^{c} (ppm)
600	9	**510**	−277	$\mathbf{4^{c}2^{c}0}$	−574	$\mathbf{3^{f}3^{f}0}$	−883	$\mathbf{2^{c}4^{c}0}$	−1204	**150**	−1538	**060**	−1882
501	669	$\mathbf{4^{t}11}$	409	$\mathbf{4^{t}2^{t}0}$	−576	$\mathbf{3^{m}3^{m}0}$	−885	$\mathbf{2^{t}4^{t}0}$	−1207	**051**	−765		
$\mathbf{4^{c}02^{c}}$	1282	$\mathbf{4^{c}11}$	405	$\mathbf{3^{f}2^{c}1}$	129	$\mathbf{2^{c}3^{f}1}$	−152	$\mathbf{14^{c}1}$	−452				
$\mathbf{4^{t}02^{t}}$	1263	$\mathbf{3^{f}12^{c}}$	1042	$\mathbf{3^{m}2^{c}1}$	134	$\mathbf{2^{t}3^{m}1}$	−155	$\mathbf{14^{t}1}$	−464				
$\mathbf{3^{f}03^{f}}$	1852	$\mathbf{3^{m}12^{c}}$	1044	$\mathbf{3^{m}2^{t}1}$	126	$\mathbf{2^{c}3^{m}1}$	−161	$\mathbf{04^{c}2^{c}}$	259				
$\mathbf{3^{m}03^{m}}$	1830	$\mathbf{3^{m}12^{t}}$	1019^{c}	$\mathbf{2^{c}2^{c}2^{t}}$	767^{c}	$\mathbf{13^{f}2^{c}}$	535	$\mathbf{04^{t}2^{t}}$	222				
$\mathbf{2^{c}04^{c}}$	2362	$\mathbf{2^{c}13^{m}}$	1618	$\mathbf{2^{c}2^{c}2^{c}}$	793	$\mathbf{13^{m}2^{c}}$	528						
$\mathbf{2^{t}04^{t}}$	2337	$\mathbf{2^{c}13^{f}}$	1642	$\mathbf{2^{t}2^{c}2^{c}}$	796	$\mathbf{13^{m}2^{t}}$	503^{d}						
105	2835	$\mathbf{2^{t}13^{m}}$	1616	$\mathbf{2^{c}2^{t}2^{c}}$	787	$\mathbf{03^{f}3^{f}}$	1184						
006	3275	**114t**	2155	$\mathbf{2^{t}2^{t}2^{t}}$	768^{c}	$\mathbf{03^{m}3^{m}}$	1152						
		114c	2177	$\mathbf{12^{c}3^{m}}$	1393								
		015	2680	$\mathbf{12^{c}3^{f}}$	1418								
				$\mathbf{12^{t}3^{m}}$	1389								
				$\mathbf{02^{c}4^{c}}$	1981								
				$\mathbf{02^{t}4^{t}}$	1955								

[a] Note that the chemical shifts of the species $\mathbf{3^{m}12^{t}}$, $\mathbf{2^{c}2^{c}2^{t}}$, $\mathbf{2^{t}2^{t}2^{t}}$, and $\mathbf{13^{m}2^{t}}$ are *predicted* from the trend analysis. [b] Code for species has been adapted from Drews and Preetz. [c] Average value ±2 ppm, since some δ^{195}Pt values differ slightly depending on the reaction conditions. [d] Predicted value, since species was not observed.

ions in the octahedral complex; the second numeral signifies the number of bromide ions, while the third numeral indicates the number of hydroxide ions coordinated to the Pt(IV) ion. 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 $[Pt(OH)_6]^{2-}$ species (**006**) was not formed at sufficient concentrations of H_2PtCl_6, to which NaOH(aq) was added (even in larger excess), to be observable in these ^{195}Pt NMR spectra, necessitating the addition of solid $Na_2[Pt(OH)_6]$. The ^{195}Pt peak attributable to **006** ($\delta^{195}Pt = 3275$) in the spectrum shown in Figure 1a is the result of such an addition.

Although Carr et al.[6] first assigned the ten possible $[PtCl_{6-n}(OH)_n]^{2-}$ ($n = 0-6$) complexes using ^{195}Pt NMR spectroscopy, we re-examined this series to obtain a consistent series of relative δ^{195}Pt values for the trend analysis discussed below. Our observed ^{195}Pt chemical shifts (measured relative to an external but coaxial reference assigned to $\delta^{195}Pt = 0.0$ ppm), given in Table 1, are in reasonably good agreement to those reported by Carr et al. Interestingly, it should be noted that the differences between our measured δ^{195}Pt values of the $[PtCl_{6-n}(OH)_n]^{2-}$ complexes compared to those reported by Carr and co-workers appears to depend on n, the number of hydroxide ions bound to Pt(IV), increasing slightly for the $[PtCl_{6-n}(OH)_n]^{2-}$ complexes with increasing n. These variations are most probably the result of the slightly different concentrations and conditions under which both studies were performed, which could be verified by a separate experiment, in which the NaOH concentration was varied at a fixed $[Pt]_f$ (0.25 M). We observe a slight dependence of the ^{195}Pt chemical shift on the OH^- concentration, increasingly so for the $[PtCl_{6-n}(OH)_n]^{2-}$ complexes with increasing n. Whereas the $[PtCl_6]^{2-}$ complex showed no significant shift in δ^{195}Pt when the OH^- concentration was increased from 0.2 to 5.0 M, the $[Pt(OH)_6]^{2-}$ resonance shifted upfield by as much as 40 ppm (from 3284 to 3245 ppm). The same upfield shift pattern was observed when $[Pt]_f$ was increased at a fixed NaOH concentration. A similar behavior was reported by Appleton et al., who found that the δ^{195}Pt of the $[Pt(H_2O)_4]^{2+}$ complex shifted in the downfield direction with increasing perchloric acid concentration, hence in the opposite direction to our findings upon addition of a base.[14] This suggests that the ionic strength/pH of the solution affects the ^{195}Pt chemical shifts of, particularly, Pt(IV) species with several hydroxy ligands to a significant extent, certainly more so than observed for the $[PtCl_{6-m}Br_m]^{2-}$ ($m = 0-6$) species.

In this context, it is also revealing to compare the reported δ^{195}Pt values of the corresponding chloroaquoplatinum(IV) complexes $[PtCl_x(H_2O)_{6-x}]^{4-x}$, as obtained by Gröning and Elding, for the oxidation of $[Pt(H_2O)_4]^{2+}$ by Cl_2 in perchloric acid.[10] The reported δ^{195}Pt (relative to $[PtCl_6]^{2-}$) for the aqua complexes $[PtCl(H_2O)_5]^{3+}$, *cis/trans*-$[PtCl_2(H_2O)_4]^{2+}$, *mer/fac*-$[PtCl_3(H_2O)_3]^{+}$, $[PtCl_4(H_2O)_2]$ [unknown isomer, *cis* or *trans*], and $[PtCl_5(H_2O)]^-$ were 2640, 2173, 2248, 1646, 1548, 1029, and 475 ppm, respectively. By comparison to our data in Table 1, the δ^{195}Pt chemical shifts for the aquated complexes differ significantly (by more that the *maximum* expected experimental error of ±10 ppm resulting from small temperature, concentration, and reference variations known to affect ^{195}Pt chemical shifts) from the corresponding *hydroxy*chloroplatinum(IV) complexes **105**, $\mathbf{2^{c}04^{c}}$, $\mathbf{2^{t}04^{t}}$, $\mathbf{3^{m}03^{m}}$, $\mathbf{3^{f}03^{f}}$, $\mathbf{4^{c}02^{c}}$, $\mathbf{4^{t}02^{t}}$, and **501** by $[\delta^{195}Pt_{(hydroxy)} - \delta^{195}Pt_{(aqua)}]$ 195, 189, 89, 184, 304, 234 (or 253 since the isomer of the $[PtCl_4(H_2O)_2]$ complex was unspecified),[10] and 194 ppm, respectively. Evidently these large differences underscore the extremely high sensitivity of the ^{195}Pt chemical shift of the Pt(IV) complexes to subtle differences in the nature of the coordinated ligands, which in this case, particularly, depend on the degree of protonation of the coordinated water molecule in the first instance and, presumably, on which geomeric isomer (where applicable) is

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considered. Given that the reported chloroaquaplatinum(IV) complexes by Gröning and Elding were examined in 2 M $HClO_4$, it is reasonable to assume little or no hydrolysis of these complexes, whereas our complexes are certainly all halo*hydroxy*platinum(II) complexes because these were all observed in strongly alkaline solutions at an initial pH > 12. Indeed, the observed chemical shift differences between the $[PtCl_x(H_2O)_{6-x}]^{4-x}$ and $[PtCl_{6-n}(OH)_n]^{2-}$ ($n = 0-5$) provide a significant justification for the present study because the extent of hydrolyis of the chloroaquoplatinum(IV) complexes in water as a function of pH has not been fully and quantitatively investigated to our knowledge.

In recent years, relatively accurate high-level computation of metal nuclei shieldings has become practical, and this field is developing rapidly with some impressive successes.[15] Nevertheless, in particular for the calculation of ^{195}Pt chemical shifts for even simple complexes such as $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$, it was recently shown by Sterzel and Autschbach that not only are very high-level and flexible computational basis sets required for reasonably accurate predictions of chemical shifts, but the importance of taking into account solvent shell structures, as well as other unspecified electronic solvent–solute interactions, should not be underestimated because these can profoundly affect the agreement between experimental and calculated ^{195}Pt chemical shifts.[16] In the case of the series of $[PtCl_{6-x}Br_x]^{2-}$ complexes, the very good agreement between the computed and experimental chemical shifts reported by Penka Fowe et al.[17] and ourselves[12] is encouraging, although as pointed out by Sterzel and Autschbach,[16] this may be the result of a fortuitous cancellation of computational errors, together with the expectation that these complexes are likely to have very similar solvation shells in water. Moreover, it appears that a continuum solvent interaction model alone cannot adequately represent the effects of solvent–solute interactions in this context. As our own preliminary computational efforts in this regard suggest, explicit single-water molecule interactions with $[PtCl_6]^{2-}$ can induce very significant effects on the computed chemical shift of this complex.[12] Moreover work in progress in our laboratory shows that, for complexes such as $[PtCl_{6-n}(OH)_n]^{2-}$, the agreement between the computed and experimental shift deteriorates significantly as the number (n) of hydroxy groups bound to platinum(IV) increases, suggesting that platinum-bound ligands such as OH^- (or H_2O) which are capable of forming strong hydrogen bonds with the water solvent or undergoing protonation/deprotonation reactions may play an important role in the determination of the experimental chemical shift of such species. Work aimed at elucidating such postulated effects is underway.

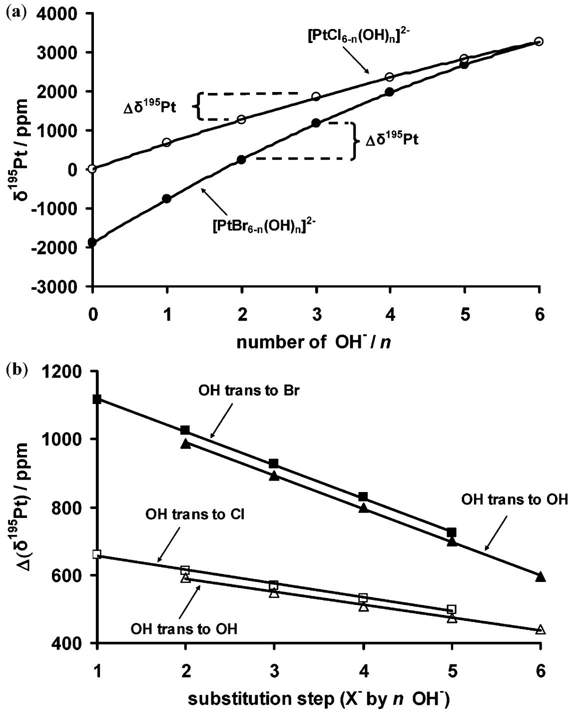

Figure 2. (a) Average ^{195}Pt chemical shifts of $[PtCl_{6-n}(OH)_n]^{2-}$ (○) and $[PtBr_{6-n}(OH)_n]^{2-}$ (●) complexes as a function of the number of hydroxide ions ($n = 0-6$) in alkaline solution of H_2PtCl_6 ($[Pt]_f = 0.38$M) and H_2PtBr_6 ($[Pt]_f = 0.50$ M). (b) Chemical shift increments ($\Delta\delta^{195}$Pt) between the $[PtCl_{6-n}(OH)_n]^{2-}$ species where Cl^- is substituted by OH^- *trans* to Cl^- ($\Delta^A\delta^{195}$Pt, □), or *trans* to OH^- ($\Delta^B\delta^{195}$Pt, △). Likewise, closed symbols indicate chemical shift increments ($\Delta^{C/D}\delta^{195}$Pt) between the $[PtBr_{6-n}(OH)_n]^{2-}$ species for the corresponding substitutions of Br^- ions by OH^- ions.

Experimentally, the replacement of Cl^- ions by OH^- ions within the coordination sphere of Pt(IV) leads to a monotonic downfield δ^{195}Pt shift with a well-defined second-order correlation of δ^{195}Pt as a function of n ($R^2 > 0.9999$), shown in Figure 2a. The chemical shift *increment*, $\Delta(\delta^{195}Pt)$, between the $[PtCl_{6-n}(OH)_n]^{2-}$ species for the substitution of Cl^- ions by OH^- ions at a position *trans* to a Cl^- ion, is well correlated through a different linear trend line ($\Delta^A(\delta^{195}Pt) = 695.8 - 40.5n$) ($n = 1-5$) as compared to that resulting from the substitution of a Cl^- ion by an OH^- ion at a position *trans* to an OH^- ion ($\Delta^B(\delta^{195}Pt) = 665.9 - 38.3n$) ($n = 2-6$) (see Figure 2b). These linear trend lines with $R^2 \approx 0.995$ allow for the assignment of all the stereoisomers because substitution of Cl^- by OH^- at a position *trans to a Cl^- ion* which systematically causes a 20–25 ppm larger $\Delta(\delta^{195}Pt)$ than substitution of Cl^- by OH^- at a position *trans to an OH^- ion*.

The above chemical shift trend analysis serves as a means for the assignment of new Pt(IV) hydroxo–halide series of complexes as illustrated by the hydroxide for bromide ion substitution study of the $[PtBr_6]^{2-}$ species, not previously

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(15) (a) Autschbach, J.; Ziegler, T. Relativistic computation of NMR shieldings and spin-spin coupling constants. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; Wiley & Sons: Chichester, U.K., 2002; Vol. 9, pp 306–323. (b) Autschbach, J. The calculation of NMR parameters in transition metal complexes. In *Principles and Applications of Density Functional Theory in Inorganic Chemistry I*; Kaltsoyannis, N., McGrady, J. E., Eds.; Springer: Heidelberg, Germany, 2004; Vol. 112, pp 1–48. (c) Autschbach, J. Calculation of heavy-nucleus chemical shifts: Relativistic all-electron methods. In *Calculation of NMR and EPR Parameters. Theory and Applications*; Kaupp, M., Bühl, M., Malkin, V. G., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 227–247. (d) Bühl, M. NMR of transition metal compounds. In *Calculation of NMR and EPR Parameters*; Kaupp, M., Bühl, M., Malkin, V. G., Eds.; Wiley-VCH: Weinheim, Germany, 2004. (e) Kaupp, M.; Malkin, V. G.; Malkina, O. L. NMR of Transition Metal Compounds. In *Encyclopedia of Computational Chemistry*; von Ragué Schleyer, P., Ed.; Wiley & Sons: Chichester, U.K., 1998.

(16) Sterzel, M.; Autschbach, J. *Inorg. Chem.* **2006**, *45* (8), 3316–3324.

(17) Penka Fowe, E.; Belser, P.; Daul, C.; Chermette, H. *Phys. Chem. Chem. Phys.* **2005**, *7* (8), 1732–1738.

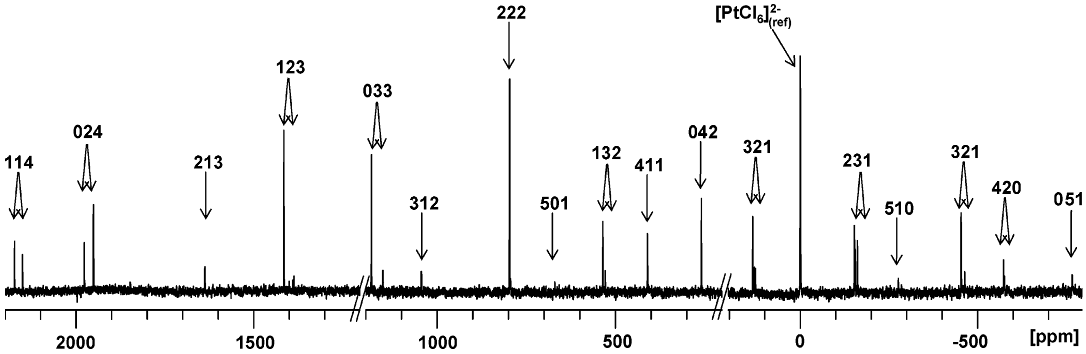

Figure 3. ^{195}Pt NMR spectra of a solution ($[Pt]_f = 0.41$ M) with equimolar quantities of H_2PtCl_6 and H_2PtBr_6, to which 2.1 molar equiv of NaOH (relative to total Pt) have been added. For clarity, the individual stereoisomers which are visible under these conditions are not indicated. Although most of the ternary $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ species are observable in this spectrum, the peak of, for example, the **501** species is too small to be visible, although it is seen at an appropriate time after mixing (see Figure 1a).

reported. The addition of 4.0 molar equiv of OH^- ions to an aqueous solution of H_2PtBr_6 rapidly results in a color change from deep red to red/brown. Inspection of the ^{195}Pt NMR spectra (Figure 1b) of this alkaline solution (pH $\approx$ 13−14) reveals all 10 expected peaks resulting from $[PtBr_{6-n}(OH)_n]^{2-}$ ($n = 0-6$) over a 5000 ppm range (note that the **006** complex was only visible after the addition of $Na_2[Pt(OH)_6]$). All the ^{195}Pt signals could be easily assigned to the various $[PtBr_{6-n}(OH)_n]^{2-}$ ($n = 0-6$) species in a manner similar to that for the $[PtCl_{6-n}(OH)_n]^{2-}$ species (see Table 1); a plot of the average δ^{195}Pt as a function of the number of substituted OH^- ions again displays a good ($R^2 > 0.9999$) second-order relationship. Similarly, the linear correlations of the $\Delta(\delta^{195}$Pt) increment versus the substitution of Br^- ions by hydroxide ions allows for the easy assignment of the individual isomers: substitutions of Br^- by OH^- at a position *trans* to Br^- or OH^- follow almost perfect ($R^2 = 0.9995$) parallel linear trend lines, with the former (OH^- *trans* to Br^-) $\Delta^C(\delta^{195}Pt) = 1218.2 - 97.9n$) ($n = 1-5$) and the latter ($OH^-$ *trans* to OH^-) $\Delta^D(\delta^{195}Pt) = 1186.0 - 97.8n$) ($n = 2-6$) (see Figure 2b). In a similar manner to that for the Pt−chloro−hydroxo complexes above, the trends for the Pt−bromo−hydroxo complexes show that substitution of Br^- by OH^- at a position *trans to a Br^- ion* systematically causes a 25−35 ppm larger $\Delta(\delta^{195}Pt)$ than substitution of Br^- by OH^- at a position *trans to an OH^- ion*.

Consistent with our recent findings in similar systems of acidic aqueous H_2PtCl_6 solutions,[7] qualitatively, the rate of ligand exchange (substitution of halide ions by OH^- ions) is found to be relatively rapid because the $[PtX(OH)_5]^{2-}$ (X = Cl or Br) signal could be detected in solution within 10 min after the addition of excess NaOH solution (3.2 and 4.0 molar equiv of OH^- ions to total Pt(IV) ions). However, in these solutions, the *extent* of the halide ion substitution by OH^- is seen to be much more pronounced, compared to that of the exchange of chloride or bromide ions by H_2O molecules in acidic media, as we reported previously,[7] pointing to a much higher affinity of OH^- ions for Pt(IV) than of water molecules. For comparison, in the most-dilute 6 mM $[Pt]_t$ acidic H_2PtCl_6 solutions, only the aquation products $[PtCl_5(H_2O)]^-$ and $[Pt(Cl_4(H_2O)_2]$ could be observed in ^{195}Pt NMR spectra, despite the ~1000-fold molar excess of water relative to $[PtCl_6]^{2-}$,[7] whereas substitution of Cl^- by OH^- takes place to yield immediately observable $[PtCl_{6-n}(OH)_n]^{2-}$ $n = 1-3$ complexes in solution when the initial molar ratio of "unbound" $OH^-/[PtCl_6]^{2-}$ is just 1:10. No quantitative studies of the relative stabilities of Pt(IV)-halo−aquo and halo−hydroxo complexes derived from the $[PtCl_6]^{2-}$ and $[PtBr_6]^{2-}$ complexes could be found in the literature, although equilibrium constants (K_{Cl}) have been reported by Leden and Chatt[18] for the Pt(II) complex $[PtCl_3(C_2H_4)]^-$ for the substitution of Cl^- by a variety of ligands (L)

$$[PtCl_3(C_2H_4)]^- + L \rightleftharpoons trans\text{-}[PtCl_2(C_2H_4)L] + Cl^- \quad (2)$$

The K_{Cl} values, determined at room temperature in aqueous solutions (relative to Cl^-) are 3×10^{-3} for L = H_2O, 3.4 for L = Br^-, and $\sim 10^6$ for L = OH^-; these findings are consistent with the findings reported here.

^{195}Pt Chemical Shift Trends for Rapid and Clear Assignments of Ternary $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ Species. The addition of a 2.1-fold molar excess of OH^- ions relative to total Pt to an equilibrated solution of equimolar amounts of H_2PtCl_6 and H_2PtBr_6, containing all ten $[PtCl_{6-m}Br_m]^{2-}$ ($m = 0-6$) species, results in the observation of over 30 separate peaks in the ±3000 ppm spectral range of the ^{195}Pt NMR spectrum shown in Figure 3, showing virtually the entire series of $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ ($m,n = 0-6$) species in solution.

Close inspection of the spectra shown in Figures 1 and 3 indicates that the *cis*/*trans* and *fac*/*mer* stereoisomers are always found within 40 ppm of each other, whereas the observed average chemical shift difference between $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ complexes of different stoichiometric composition is typically ≥100 ppm. This serves as a starting point for the assignment of all ^{195}Pt resonances as shown by the hypothetical ligand substitution scheme for the total of 56 unique $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ complexes possible (Scheme 1).

The scheme displays the complexes arranged according to increasing number of coordinated Br^- ions from left to right, showing the $[PtCl_{6-m}Br_m]^{2-}$ species in the top row. Species with the same number of Br^- ions are shown grouped

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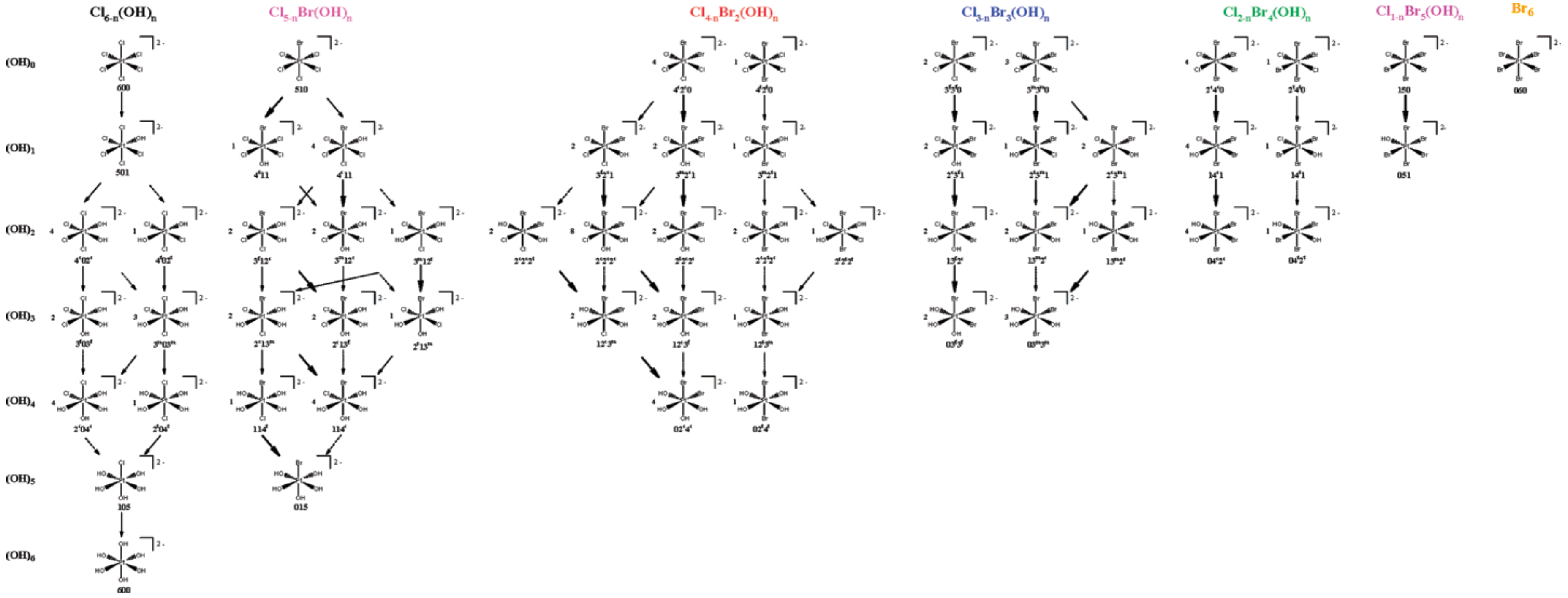
[18] Leden, I.; Chatt, J. *J. Chem. Soc.* **1955**, 2936.

Scheme 1. Reaction Scheme for the Stepwise Replacement of Cl^- in $[PtCl_{6-m}Br_m]^{2-}$ ($m = 0-6$) Complexes with nOH^- ($n = 0-6$)[a]



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[a] The designation of species has been adapted from Drews and Preetz.[13] The bold numbers to the left of the species represent the statistically expected isomer ratio, when applicable. Bold, full, and dashed arrows represent substitutions of Cl^- by OH^- at a position *trans* to a Br^- ion, *trans* to a Cl^- ion, and *trans* to an OH^- ion, respectively (*not* all possible substitution pathways are shown in the interest of clarity, see text).

together, with the stepwise substitution of chloride ions by hydroxide ions indicated from top to bottom. Other possible direct conversions (such as the substitution of Br^- ions by OH^- ions, e.g., **231** → **222** → **213**, etc.) are omitted in Scheme 1 for clarity. The bold numerals to the left of the species represent the statistically expected isomer ratio, when applicable, not taking the consequences of the kinetic *trans* effect into account. Bold, full and dashed arrows represent substitutions of Cl^- by OH^- at a position *trans* to a Br^- ion, *trans* to a Cl^- ion, and *trans* to an OH^- ion, respectively. Substitutions *trans* to a Br^- ion are expected to show the largest *trans effect* of the three types of substitutions.[13,19,20] This implies that substitutions of Cl^- by OH^- at a position *trans* to a Br^- ion are *kinetically* favored over those *trans* to a coordinated Cl^- ion, which in turn, are expected to be kinetically favored over replacements of Cl^- by OH^- at a position *trans* to an OH^- ion. The ^{195}Pt NMR spectra were deliberately recorded under dynamic conditions before solutions had reached a steady state, so that the observable distribution of species (as well as the relative concentrations of species) was *time-dependent* and determined mainly by kinetic rather than thermodynamic factors. Hence the *trans* effect[20,21] may be invoked for an initial plausible assignment of the ^{195}Pt resonances to species. As will be shown below, the full chemical shift trend analysis confirms the correct assignment of these species in solution.

In this way, it is possible to observe 52 of the 56 complexes, 33 of which have not been previously characterized by ^{195}Pt NMR nor by any other analytical method, with the exception of the $[PtBr_4(OH)_2]^{2-}$ complex.[22] Figure 4 illustrates the chemical shift trend analysis which confirms our assignment of all $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ species; a plot, using the same hierarchical designation as in Scheme 1, of the average δ^{195}Pt of the $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ complexes as a function of the number of coordinated hydroxide ions is shown, whereby each line represents a series of complexes with an identical number of bromide ions (Figure 4).

The excellent ($R^2 > 0.9999$) second-order correlations of the remarkable set of slightly curved, but virtually parallel, chemical shift trends to the line observed for the $[PtCl_{5-n}Br(OH)_n]^{2-}$ series of complexes (line for $m = 0$, Figure 4a), is strong confirmation that the complexes with identical ligand stoichiometry are "grouped" correctly. For example, the $[PtCl_{5-n}Br(OH)_n]^{2-}$ species are correlated through the line for $m = 1$ (Figure 4a): $\delta^{195}\text{Pt} = -273.8 + 697.1n - 21.4n^2$ from which, using an integral value of n in the range 0−5, the average δ^{195}Pt for any particular species with a defined number of Cl^-, Br^-, and OH^- ions may be predicted to within 0.2% of the observed average δ^{195}Pt values. In this way, the ^{195}Pt resonance at 409 ppm (Figure 3) can easily be assigned to one of the two possible (*cis* or *trans*) **411** $[PtCl_4Br(OH)]$ isomers. In a similar fashion, the small resonance at 1044 ppm can be assigned to one of the **312** isomers, whereas the resonance at 1642 ppm, is attributed to a **213** species. Finally, the peaks at 2155 and 2177 ppm are attributable to isomers of the **114** species, with the signal at 2680 ppm assigned above to **015** (see Figure 1b).

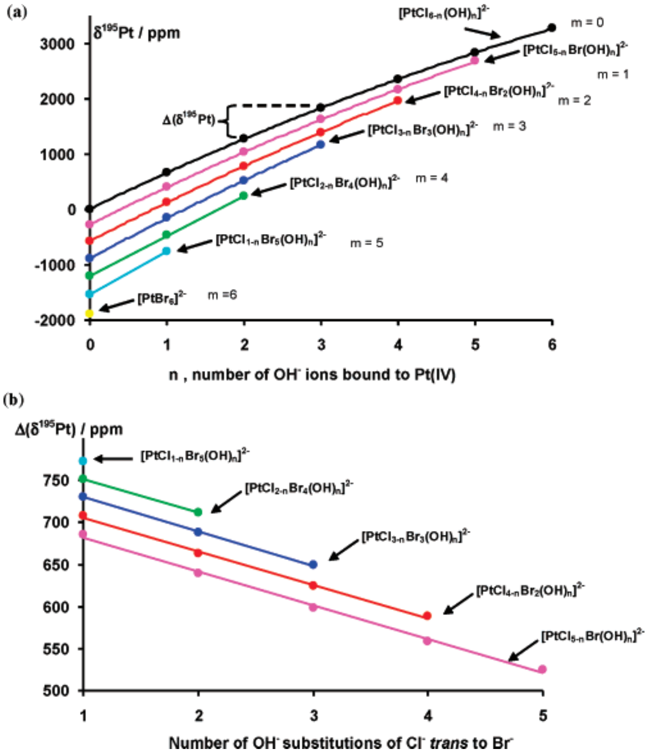

Figure 4. (a) Average ^{195}Pt chemical shifts of $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ complexes (black, $m = 0$; pink, $m = 1$; red, $m = 2$; blue, $m = 3$; green, $m = 4$; aqua, $m = 5$; yellow, $m = 6$) plotted as a function of the number of n hydroxide ions ($n = 0-6$). (b) Chemical shift increments for the substitution of Cl^- by n hydroxide ions ($n = 1-6$) at a position trans to Br^- in $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ complexes (black, $m = 0$; pink, $m = 1$; red, $m = 2$; blue, $m = 3$; green, $m = 4$; aqua, $m = 5$).

To assign the geometrical isomers of species correctly, it turns out that the expected differences in the *trans* effect for the substitutions of Cl^- by OH^- occurring at positions *trans* to Br^-, Cl^-, or OH^- (the bold, full, and dashed arrows, respectively) can be invoked to distinguish these isomers. This may be illustrated by the observation that immediately after addition of NaOH solution to the H_2PtCl_6/H_2PtBr_6 mixture, only the *trans*-$[PtCl_4Br(OH)]^{2-}$ isomer **4^{t}11** is visible as a resonance at 409 ppm in the series of $[PtCl_{5-n}Br(OH)_n]^{2-}$ species (Figure 5a), while a resonance of lower intensity at 405 ppm (*not* shown in Figure 5a) becomes visible only several hours after the NaOH addition, which may be assigned to the **4^{c}11** species based on differences in the relative *trans* effect for the isomers; the **4^{t}11** isomer is expected to be formed more rapidly, although it also disappears at a slower rate (as a result of further substitution) than the **4^{c}11** complex (Scheme 1). This results in the assignment of the resonances at 409 and 405 ppm to the **4^{t}11** and **4^{c}11** species, respectively.

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[22] (a) Al'Ansari, S. V.; Zheligovskaya, N. N.; Chernova, N. A. *Russ. J. Coord. Chem.* **1995**, *21* (7), 547−550. (b) Budanova, N. S.; Zheligovskaya, N. N.; Spitsyn, V. I.; Glazunov, P. Y. *B. Acad. Sci. USSR* **1975**, No. 12, 2658−2660. (c) Zheligovskaya, N. N.; Al Ansari, S. V. *Koordinats. Khim.* **1983**, *9* (7), 962−964.

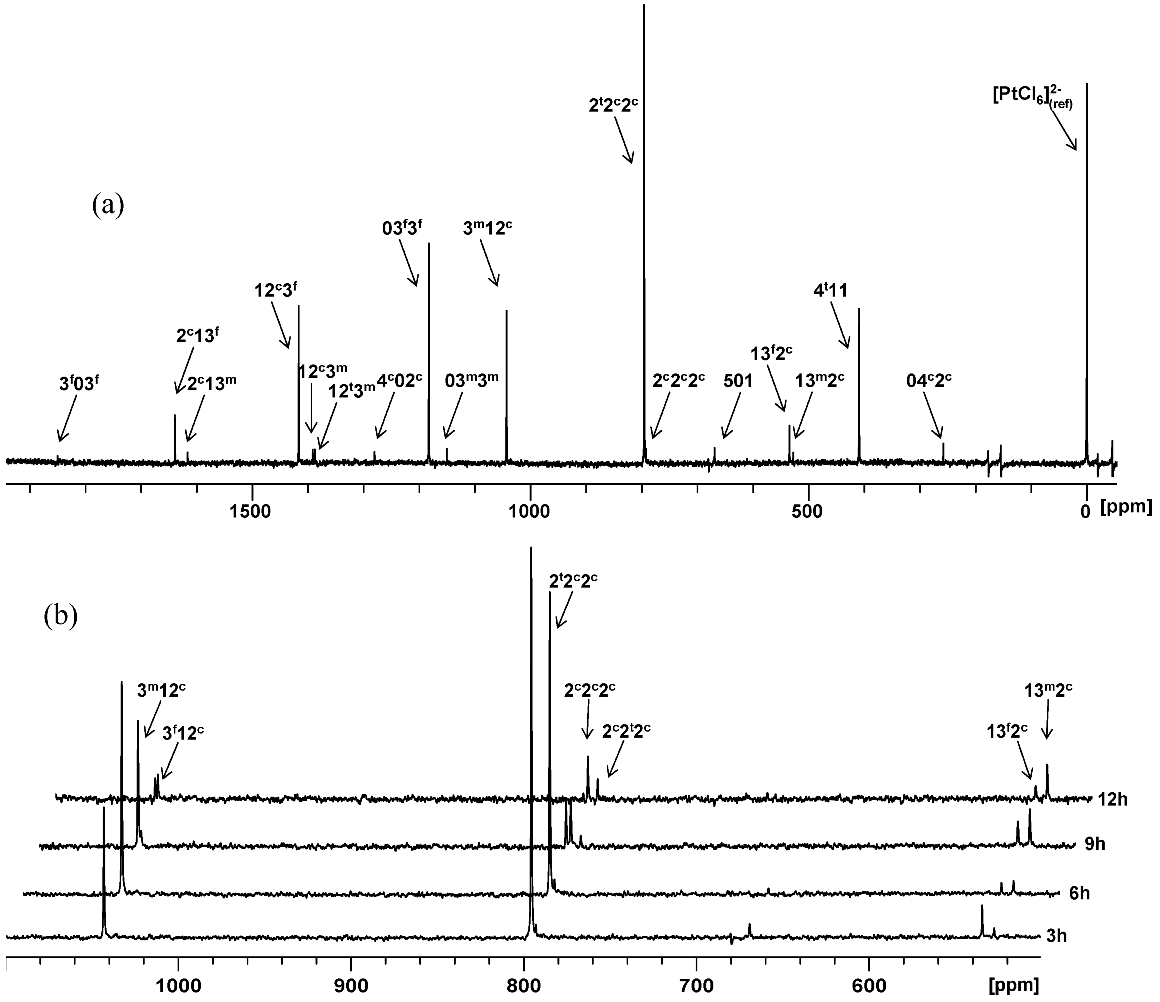

Figure 5. ^{195}Pt NMR spectra of an aged solution with a 2:1 mole ratio of H_2PtCl_6/H_2PtBr_6 with 3.2 molar equiv of NaOH ($[Pt]_f = 0.38$ M) added, recorded at 3 h intervals to monitor changes in stereoisomer distribution over time: (a) spectrum obtained after 3 h in the δ^{195}Pt range of 1950 to −50 ppm. (b) A detailed view of the spectra over successive 3 h time intervals showing changes in distribution of stereoisomer of the $[PtCl_3Br(OH)_2]^{2-}$, $[PtCl_2Br_2(OH)_2]^{2-}$, and $[PtClBr_3(OH)_2]^{2-}$ complexes. (Inverted signals are "folded" peaks from the low-field end of the spectrum.)

Figure 5b shows a detailed view of ^{195}Pt spectra acquired over 3 h time intervals to enable the visualization of relative species distribution changes in time, while obtaining spectra with sufficient signal/noise to observe the complexes present in low concentration. Considering for example the $[PtCl_3Br(OH)_2]^{2-}$ species (trend line for $m = 1$) and applying the same reasoning as for the two **411** isomers above, we expect the $\mathbf{3^{m}12^{c}}$ complex to be kinetically favored over the $\mathbf{3^{f}12^{c}}$ species, whereas the third stereoisomer $\mathbf{3^{m}12^{t}}$ will be least readily observable. This is confirmed by Figure 5b, which clearly shows that during the first 6 h after solution preparation, only one isomer, the $\mathbf{3^{m}12^{c}}$ at $\delta^{195}\mathrm{Pt} = 1044$ ppm, is seen, followed by the later appearance of a resonance at $\delta^{195}\mathrm{Pt} = 1042$ ppm assigned to the isomer $\mathbf{3^{f}12^{c}}$. The $\mathbf{3^{m}12^{t}}$ isomer could not be seen in these solutions, while both the $\mathbf{3^{m}12^{c}}$ and $\mathbf{3^{f}12^{c}}$ species show only transient existence in solution and are in turn converted into the $[PtCl_2Br(OH)_3]^{2-}$ isomer $\mathbf{2^{c}13^{f}}$ at 1642 ppm (Scheme 1 and Figure 5a). Even more striking is the change in the relative concentrations of the $[PtCl_2Br_2(OH)_2]^{2-}$ isomers over a 12 h period. During the first 6 h, the $\mathbf{2^{t}2^{c}2^{c}}$ stereoisomer is almost exclusively present ($\delta^{195}\mathrm{Pt} = 796$ ppm, Figure 5b) because of the large *trans* effect for substitution of Cl^- by OH^- in the conversions $\mathbf{4^{c}2^{c}0} \rightarrow \mathbf{3^{m}2^{c}1} \rightarrow \mathbf{2^{t}2^{c}2^{c}}$. After 12 h, a resonance at 793 ppm becomes dominant, which is assigned to the $\mathbf{2^{c}2^{c}2^{c}}$ complex because this isomer is expected to form more slowly than the $\mathbf{2^{t}2^{c}2^{c}}$ isomer at $\delta^{195}\mathrm{Pt} = 796$ ppm. Concomitantly, a third isomer peak appears at 787 ppm, which has been identified as $\mathbf{2^{c}2^{t}2^{c}}$, in agreement with the reaction scheme. Unfortunately resonances ascribable to the other two isomers of $[PtCl_2Br_2(OH)_2]^{2-}$ ($\mathbf{2^{c}2^{c}2^{t}}$ and $\mathbf{2^{t}2^{t}2^{t}}$) could not be observed under these dynamic spectral acquisition conditions, which is understandable in terms of the very low *trans effect* of OH^- resulting in negligible formation over this time period of species in which OH^- ions are *trans* to each other. Significantly, the other two isomers of $\mathbf{3^{m}12^{t}}$ $[PtCl_3Br(OH)_2]^{2-}$ and $\mathbf{13^{m}2^{t}}$ $[PtClBr_3(OH)_2]^{2-}$, which could also not be observed under any conditions in our solutions, contain two hydroxide ions *trans* to each other, and so, they account for the "missing" 4 out of 56 possible complexes in our solutions, although their expected chemical shifts can readily be predicted (vide infra).

In this way, virtually all the observable isomers of $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ complexes can be easily assigned by

Table 2. ^{195}Pt Chemical Shift Increment Trend Correlation Data for the Substitution of Cl^- by n OH^- at a Position *trans* to Br^-, Cl^-, or OH^- in $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ Complexes[a]

complex	ligand trans to OH^-		
	Br^-	Cl^-	OH^-
$[PtCl_{6-n}(OH)_n]^{2-}$		$695.8 - 40.5n$ $n = 1-5$, $R^2 = 0.9949$	$665.9 - 38.3n$ $n = 2-5$, $R^2 = 0.9955$
$[PtCl_{5-n}Br(OH)_n]^{2-}$	$722.1 - 40.2n$ $n = 1-5$, $R^2=0.9967$	$719.5 - 40.1n$ $n = 1-4$, $R^2 = 0.9972$	$686.6 - 37.1n$ $n = 2-5$, $R^2 = 0.9982$
$[PtCl_{4-n}Br_2(OH)_n]^{2-}$	$745.5 - 39.8n$ $n = 1-4$, $R^2 = 0.9978$	$742.0 - 40.3n$ $n = 1-3$, $R^2 = 0.9990$	$715.1 - 37.8n$ $n = 2-4$, $R^2 = 0.9996$
$[PtCl_{3-n}Br_3(OH)_n]^{2-}$	$770.7 - 40.8n$ $n = 1-3$, $R^2 = 0.9994$	$765.0 - 41.0n$ $n = 1-2$	$744.0 - 40.0n$ $n = 2-3$
$[PtCl_{2-n}Br_4(OH)_n]^{2-}$	$793.0 - 41.0n$ $n = 1-2$	743 $n = 1$	686 $n = 1$
$[PtCl_{1-n}Br_5(OH)_n]^{2-}$	773.0 $n = 1$		

[a] These may be used to predict chemical shifts for any desired ternary complex in these solutions.

a similar trend analysis approach as verified above for the $[Pt(Cl_{6-n}(OH)_n]^{2-}$ and $[PtBr_{6-n}(OH)_n]^{2-}$ ($n = 0-6$) series of complexes shown in Figure 2. Almost perfectly linear trend lines ($R^2 > 0.995$), correlating families of complex Pt(IV) species, are obtained in all cases, which strongly supports the correctness of the respective δ^{195}Pt assignments. Figure 4b shows a plot of the $\Delta(\delta^{195}Pt)$ values for the substitution of Cl^- by OH^- at a position *trans* to Br^-. In excellent agreement with the incremental shift principle shown to hold for the single halide $[PtX_{6-n}(OH)_n]^{2-}$ complexes described above, substitution of Cl^- by OH^- at a position *trans to a Br^- ion* causes a $\Delta(\delta^{195}Pt)$ consistently ~25−30 ppm larger than substitution of Cl^- by OH^- at a position *trans to an OH^- ion*. Substitution *trans* to a Cl^- ion also consistently results in, albeit slightly smaller, shift increments of 2−9 ppm, as compared to substitution *trans* to a Br^- ion.

Similar plots (not shown) of $\Delta(\delta^{195}Pt)$ values for the substitution of Cl^- by OH^- at a position *trans* to Cl^- or OH^- produce lines with equally good linear correlations. In summary, the linear correlations for all the ^{195}Pt chemical shift data for each family of complexes are listed in Table 2. These trends may be used to predict the ^{195}Pt chemical shifts of the four complex isomers which could not be directly observed in our solutions, namely, $\mathbf{3^{m}12^{t}}$ at $\delta^{195}Pt = 1019$ ppm, $\mathbf{2^{c}2^{c}2^{t}}$ at $\delta^{195}Pt = 767$ ppm, $\mathbf{2^{t}2^{t}2^{t}}$ at $\delta^{195}Pt = 768$ ppm, and $\mathbf{13^{m}2^{t}}$ at $\delta^{195}Pt = 503$ ppm. This demonstrates the utility of this approach in assigning ^{195}Pt chemical shifts for such complexes. The full list containing all the assigned $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ complexes (including only 4 predicted shifts) is given in Table 1.

It should be noted that we find no evidence in our ^{195}Pt NMR spectra for any polynuclear hydroxo-bridged species such as dimeric and trimeric Pt species with four-membered $Pt(OH)_2Pt$ rings (hydroxo-bridged complexes) that have been reported in literature.[14,23] In any event, these polynuclear complexes have in general markedly different δ^{195}Pt values compared to their corresponding mononuclear species. Moreover, because all detectable ^{195}Pt NMR resonances in our spectra could be satisfactorily assigned to the complexes listed in Table 1, we conclude that polynuclear species either do not exist under the conditions in our solutions or that they may be present at a level well below the limits of detection of high-field ^{195}Pt NMR spectroscopy in our relatively dilute solutions.

Finally, an interesting, if at first unexpected, phenomenon pertaining to the strongly alkaline solutions examined here was the observation that upon storage of these solutions directly in the NMR tubes without specific precautions, the ^{195}Pt resonances attributed to the hydroxyl-substituted Pt(IV) complexes slowly disappeared from the spectra, after later re-examination of the these solutions. In the ^{195}Pt NMR spectra recorded during the first few hours after NaOH addition to pH ~12−13, there is a rapid and significant increase in the relative concentration of $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ species with higher n, following the relatively rapid OH^- substitution of halide ions from the coordination sphere of Pt(IV). However, if these solutions are re-examined 24 h after NaOH addition, the halide complexes $[PtCl_{6-m}Br_m]^{2-}$ again begin to dominate the ^{195}Pt NMR spectrum, suggesting that halide anation reactions (by halide ions displaced by OH^- ions initially) take place. (The concomitant color change from deep orange/red to light orange/brown back to orange/red is consistent with the dynamic nature of these solutions.) This might at first appear to be rather surprising because the addition of a large molar excess of either NaBr or NaCl to a fresh aqueous solution of authentic $Na_2[Pt(OH)_6]$ does not result in the formation of any detectable quantities of $[PtX_{6-n}(OH)_n]^{2-}$ complexes when monitored by ^{195}Pt NMR over a period of several weeks. Similar "irreversibility" of OH^--substitution reactions has also been observed for the Pt(II) complexes $[PtCl_{4-n}(OH)_n]^{2-}$ complexes,[24] implying a relatively high thermodynamic stability, as well as kinetic inertness to substitution of Pt(II/IV)-hydroxo complexes. In our solutions, we find that this phenomenon is essentially pH dependent. Thus, after the addition of concentrated NaOH to solutions of $[PtCl_{6-m}Br_m]^{2-}$ complexes, the pH of the initially strongly alkaline (pH ~12−13) solution declines to pH ~7−8 upon storage over a 24 h time period without specific exclusion of air. This suggests that atmospheric CO_2 is absorbed by the strongly alkaline solutions containing the $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ species through the ethylvinylacetate stopper of the NMR tube, resulting in the regeneration of $[PtCl_{6-m}Br_m]^{2-}$ complexes in the final almost pH neutral solutions. Presumably as the pH of the solution declines as a result of carbonic acid absorption/formation, protonation of the kinetically inert hydroxyl substituted $[PtCl_{5-n}Br(OH)_n]^{2-}$ complexes results in the formation of the corresponding much more-labile aquated complexes, which then react with the relative excess of halide ions present in solution, resulting in the $[PtCl_{6-m}Br_m]^{2-}$ complexes becoming predominant in

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(23) (a) Agnew, N. H.; Appleton, T. G.; Hall, J. R. *Aust. J. Chem.* **1982**, *35* (5), 881−894. (b) Boreham, C. J.; Broomhead, J. A.; Fairlie, D. P. *Aust. J. Chem.* **1981**, *34* (3), 659−664.

(24) Wu, L.; Schwederski, B. E.; Margerum, D. W. *Inorg. Chem.* **1990**, *29* (18), 3578−3584.

neutral solutions again. This emphasizes the dynamic nature of the speciation study carried out here. Although this interesting observation requires more detailed investigation, support for this hypothesis is obtained when thoroughly argon-degassed solutions were used instead and by performance of the NaOH additions in a Schlenk tube under argon. Solutions protected from exposure to atmospheric gases and kept under Ar in the NMR tube remained at their initial high pH, and the distribution of $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ species remains stable for several weeks.

Concluding Remarks

Dynamic ^{195}Pt NMR experiments carried out together with the corresponding internally consistent chemical shift trend analysis is a powerful method for the rapid assignment of nearly all of the 56 $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ complexes (m, n = 0−6), including where possible, their respective geometrical isomers. In this manner, 33 new species have been identified and characterized by their ^{195}Pt chemical shifts. The chemical shift trend analysis is based on the fact that the average δ^{195}Pt of $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ species displays excellent *second-order* correlations when plotted as a function of the number of hydroxide ions for families of complexes. The remarkably *linear* relationships between the chemical shift increments, $\Delta(\delta^{195}Pt)$, induced by substitution of Cl^- ions by n OH^- ions allows for the virtually unambiguous assignment of all stereoisomers of this series of complexes. The $\Delta(\delta^{195}Pt)$ for substitutions of Cl^- by OH^- at a position *trans* to Br^- is consistently slightly larger than at a position *trans* to Cl^- and significantly larger (by 25−30 ppm) than at a position *trans* to OH^-. The observed relative peak intensities of the stereoisomers, under dynamic conditions, are largely determined by the differences in the *trans* effect of the ligand for which a *trans* substitution takes place in the coordination sphere of the Pt(IV) complex. As a result of the small *trans* effect leading to the formation of species where hydroxide ions are at a position *trans* to each other, only four stereoisomers (**3^m12^t**, **$2^c2^c2^t$**, **$2^t2^t2^t$**, and **13^m2^t**) could not be observed under any of our conditions. However, their ^{195}Pt chemical shifts can be predicted with reasonable certainty from the linear $\Delta(\delta^{195}Pt)$ trend lines obtained for related observable species in a particular series of complexes.

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