Discussion

The importance of hydroxo-bridged complexes in the aqueous solution chemistry of platinum(II) has only begun to be recognized in recent years.[4,14-17] If our assignments are correct, we have shown that hydroxo-bridged complexes such as II, XIII, and XIX can be present in weakly acidic solutions (pH 2.5-5) as well as in neutral or alkaline solutions. Furthermore, the unsymmetrically bridged complexes XIII and XIX can be major components in the mixture of complexes in solution.

XIII does not appear to contribute much to the formation of blue colors in phosphate solutions, since near pH 6, where this is the dominant species, only weak blue colors are formed. In strongly acid solutions (pH <2), blues do not form. Coordinated unidentate phosphate is diprotonated, which inhibits bridging. From ^{31}P spectra, oligomeric phosphate-bridged species are formed most readily at pH 3-4, presumably via XII. These are also optimum conditions for formation of "blues".

From our results, it is evident that phosphato and acetato complexes will certainly be present in significant quantities in any solution of I buffered with acetate or phosphate buffers—long before any solid complexes, blue or colorless, precipitate. We would therefore suggest that results from experiments where such buffers have been used (e. g., a recent UV spectrophotometric study of the kinetics of dimerization of I[32]) be interpreted with caution.

Acknowledgment. We thank the Australian Research Grants Scheme for financial support and Dr. I. J. McMahon for some experimental assistance.

Registry No. I, 20115-64-4; II, 91994-73-9; III, 91994-74-0; IV, 41575-87-5; V, 86493-49-4; VIII, 67063-11-0; X, 91994-75-1; XI, 91994-76-2; XII, 91994-77-3; XIII, 91994-78-4; XV, 91994-79-5; XVII, 91994-80-8; XVIII, 91994-81-9; XIX, 91994-82-0; XX, 91994-84-2; *cis*-$[Pt(NH_3)_2(H_2O)_2]SO_4$, 63632-03-1; Pd(en)(PO_4H), 91994-85-3; [Pd(en)$(H_2O)_2](NO_3)_2$, 62418-53-5; *cis*-$Pt(NH_3)_2Cl_2$, 15663-27-1; $(Pt(NH_3)_2(OH))_2(\mu\text{-}OH)^+$, 91994-86-4; $Pt(NH_2CH_3)_2(PO_4H_2)(H_2O)^+$, 91994-87-5; $Pt(NH_2CH_3)_2(PO_4H)(H_2O)$, 92009-84-2; $(Pt(NH_2CH_3)_2(H_2O))_2(PO_4H)^{2+}$, 91994-88-6; $(Pt(NH_2CH_3)_2)_2(\mu\text{-}OH)(\mu\text{-}PO_4H)^+$, 91994-89-7; Pt(en)$(PO_4H_2)(H_2O)^+$, 91994-90-0; Pt(en)$(PO_4H)(H_2O$, 91994-91-1; (Pt(en)$(H_2O))_2(PO_4H)^{2+}$, 92009-85-3; *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](NO_3)_2$, 78022-63-6; ^{15}N, 14390-96-6; ^{195}Pt, 14191-88-9.

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Reactions of Platinum(II) Aqua Complexes. 2. ^{195}Pt NMR Study of Reactions between the Tetraaquaplatinum(II) Cation and Chloride, Hydroxide, Perchlorate, Nitrate, Sulfate, Phosphate, and Acetate[1]

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Complexes formed in solution between $Pt(H_2O)_4^{2+}$ (I) and anionic ligands A^{m-}, $Pt(A)_n(H_2O)_{4-n}^{(2-mn)+}$, have been characterized by ^{195}Pt NMR spectra ($A^{m-} = Cl^-$ (n = 1-4), ONO_2^- (n = 1-3), OSO_3^{2-} (n = 1, 2), $OPO_3H_2^-$ (n = 1-4), and $O_2CCH_3^-$ (n = 1)). No distinct perchlorato complexes were observed. An alkaline solution gave a single resonance assigned to $Pt(OH)_4^{2-}$. Concentrated solutions disproportionated to Pt and $Pt(OH)_6^{2-}$. Peroxide oxidation of acid and alkaline solutions gave respectively "$PtO_2 \cdot 3H_2O$" and $Pt(OH)_6^{2-}$.

Introduction

In 1976, Elding[2] reported the first preparation of solutions of the tetraaquaplatinum(II) cation, $Pt(H_2O)_4^{2+}$ (I), by reaction of K_2PtCl_4 with either silver perchlorate under controlled conditions or mercuric nitrate. Since then, the kinetics of anation of I by chloride and bromide have been studied in detail,[3,4] and its use as a starting material in the synthesis of bis(β-diketonato)platinum(II) complexes has been reported.[5] Shipachev et al.[6] prepared solutions of I by ferrous ion reduction of PtF_6^{2-} in perchloric acid and reported its ^{195}Pt chemical shift. More recently, the ^{195}Pt shift of I has been shown to be affected by the substitution of ^{18}O for ^{16}O in the coordinated water molecules.[7] Kinetics of exchange between solvent and coordinated water have been studied.[7]

In this work, we have studied equilibria 1, using ^{195}Pt NMR, where A^{m-} is an oxygen-donor ligand.

$$\underset{\text{I}}{Pt(H_2O)_4^{2+}} + nA^{m-} \rightleftharpoons Pt(A)_n(H_2O)_{4-n}^{(2-mn)+} + nH_2O \quad (1)$$

We have recently characterized by ^{195}Pt and ^{15}N NMR the complexes formed between oxygen-donor anions and *cis*-$Pt(^{15}NH_3)_2(H_2O)_2^{2+}$.[8]

Although all of the complexes in the series $PtCl_n(H_2O)_{4-n}^{(2-n)+}$ have been previously characterized by their electronic spectra,[2,9] ^{195}Pt chemical shifts have not been reported for $PtCl(H_2O)_3^+$ and *cis*-$PtCl_2(H_2O)_2$. We have measured these shifts to complete the series, so that trends as

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Table I. ^{195}Pt Chemical Shifts[a] of Nitrate, Sulfate, Phosphate, Acetate, and Chloride Complexes of $Pt(H_2O)_4{}^{2+}$

	complexes			
anion	mono	bis (cis and trans)	tris	tetrakis
$NO_3{}^-$	−24	−57 −59	−96	
$SO_4{}^{2-}$	+74	+133 +164		
$H_2PO_4{}^-$	+145	+267 +292	+424	+602
CH_3COO^-	−20			
Cl^-	−350	−811 (cis) −644 (trans)	−1185	−1625

[a] Measured relative to an aqueous solution of Na_2PtCl_6.

chloride successively replaces water may be determined and compared with trends for the O-donor ligands.

Experimental Section

$K_2Pt(OH)_6$ was prepared by the method of Maltese and Orville-Thomas.[10]

Preparation of Solutions of $[Pt(H_2O)_4](ClO_4)_2$ (I) for NMR Studies. Solutions approximately 10^{-2} M in $[Pt(H_2O)_4](ClO_4)_2$ in 1 M $HClO_4$ (with ~2 × 10^{-2} M $KClO_4$) were prepared from K_2PtCl_4 and silver perchlorate by Elding's method.[2] These solutions were too dilute for convenient NMR measurements. A 2-mL sample of ~0.2 M $[Pt(H_2O)_4](ClO_4)_2$ in 1 M $HClO_4$ was prepared as follows.

To 100 mL of dilute (10^{-2} M) solution was added 1 M NaOH solution to bring the pH to 7, precipitating $Pt(OH)_2 \cdot nH_2O$.[2] This solid was initially white but in contact with the mother liquor acquired a greenish brown color. It was separated by centrifugation and then washed three times with water, to remove soluble salts as much as possible. It was then dissolved in 2 mL of 1 M $HClO_4$ solution, and the bright yellow solution was filtered. More dilute solutions could be obtained by dilution with 1 M $HClO_4$. More concentrated solutions could be obtained by precipitating $Pt(OH)_2 \cdot nH_2O$ from larger volumes of the 10^{-2} M solution and redissolving in $HClO_4$ solution.

Determination of Concentration of $[Pt(H_2O)_4](ClO_4)_2$. The following procedure was used to determine concentration in a solution approximately 0.2 M in $Pt(H_2O)_4{}^{2+}$ and 1 M in $HClO_4$ (as used in a typical NMR experiment).

One milliliter of the solution was pipetted into a 5-mL volumetric flask, and 1 M HCl solution was added to make up to the mark. The solution was transferred to a stoppered 25-mL conical flask and heated on a boiling steam bath for 1.5 h, to ensure complete conversion to $PtCl_4{}^{2-}$. The solution was allowed to cool and its absorbance measured at 390 nm. Concentration was determined by interpolation on a Beer's law plot obtained with use of standard solutions of K_2PtCl_4 in 1 M HCl. Some undesirable oxidation to platinum(IV) tended to occur if the HCl concentration was much greater than 1 M or if solutions with high platinum concentration were heated.

Reaction of $[Pt(H_2O)_4](ClO_4)_2$ with Peroxide. One milliliter of a 0.25 M $[Pt(H_2O)_4](ClO_4)_2$ solution was treated with 0.5 mL of 30% hydrogen peroxide at 60 °C for 10 min. A yellow-orange solid was formed, which was separated by centrifugation, washed with water and then acetone, and then dried in a vacuum desiccator over silica gel for 24 h. This compound was quite different in appearance from the greenish yellow $PtO_2 \cdot 4H_2O$ ($H_2Pt(OH)_6$), formed by acidification of a solution of $K_2Pt(OH)_6$.[10,11] The compound was analyzed as $PtO_2 \cdot 3H_2O$. Anal. Calcd: Pt, 69.4; H, 2.1. Found: Pt, 69.4; H, 2.1.

Spectra. ^{195}Pt (21.4 MHz) and ^{31}P (40.3 MHz) NMR spectra were run as previously described,[8] without proton decoupling.

Results

^{195}Pt chemical shifts are listed in Table I.

Solutions of $[Pt(H_2O)_4](ClO_4)_2$ with Perchloric Acid and Sodium Perchlorate. Shipachev et al.[6] reported that the ^{195}Pt chemical shift of I changed from −35 ppm (relative to H_2PtCl_6) in 0.5 M $HClO_4$ to +75 ppm in 2 M $HClO_4$ (using the usual convention that shifts to lower shielding are positive). To check this, we examined the effect of $HClO_4$ and $NaClO_4$ on the ^{195}Pt resonance.

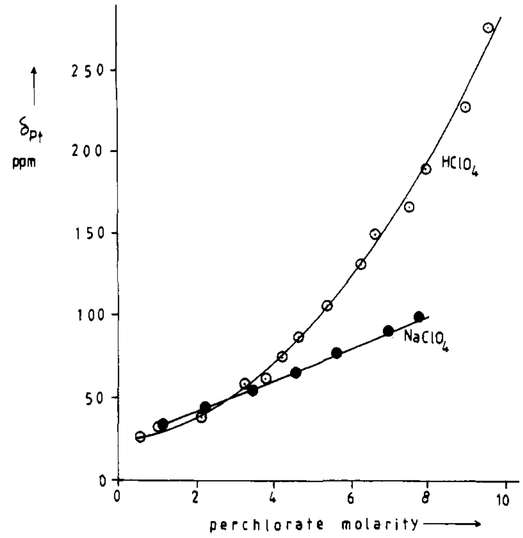

Figure 1. Dependence of ^{195}Pt chemical shift of $Pt(H_2O)_4{}^{2+}$ (I) on (●) $NaClO_4$ concentration and (⊙) "free" $HClO_4$ concentration.

Samples were prepared with differing $HClO_4$ concentrations. The concentration of I was determined spectrophotometrically after conversion to $PtCl_4{}^{2-}$. "Total acid" content was determined by titration with standard NaOH solution to a phenolphthalein end point. It was assumed that each $Pt(H_2O)_4{}^{2+}$ ion gave two protons in the titration, so that "free perchloric acid" concentration was estimated as total acid less twice the concentration of I.

In a parallel study, the effect of added $NaClO_4$ on the spectrum was determined, with $HClO_4$ concentration constant at 1 M.

In each spectrum, only one ^{195}Pt resonance was observed, up to perchlorate concentrations of 8–10 M. Since exchange of coordinated water of I with solvent water is slow on the NMR time scale,[7] it is unlikely that there would be rapid interconversion between I and a perchlorato complex. The result is therefore interpreted as indicating that there are no detectable perchlorato complexes formed in aqueous solution.

The variation in ^{195}Pt chemical shift is shown in Figure 1. Added $NaClO_4$ caused a shift to lower shielding, with a linear dependence on $NaClO_4$ concentration up to 8 M, where the shift was almost +70 ppm. A shift of this magnitude is not unexpected in view of the large changes in environment of the $Pt(H_2O)_4{}^{2+}$ ion, with ion pairing and other cation–anion interactions becoming increasingly important in the concentrated salt solutions.

With $HClO_4$, our results did not agree with those reported by Shipachev et al.[6] Over the concentration range 0.5–2.0 M, we found a shift of only +20 ppm, paralleling the change for $NaClO_4$. With $HClO_4$ concentrations above 3 M, however, the platinum nucleus is much less shielded than in corresponding $NaClO_4$ solutions (Figure 1). It did occur to us that $Pt(H_2O)_4{}^{2+}$ could be a very strong acid, only fully protonated in concentrated $HClO_4$ solutions, giving the observed shift. Titration curves show no inflection in the pH range 0–3, which could correspond to the protonation reaction (2), from which

$$Pt(OH)(H_2O)_3{}^+ + H^+ \rightleftharpoons Pt(H_2O)_4{}^{2+} \qquad (2)$$

$$Pt(OH)_2 \cdot nH_2O(s) + H^+ \rightleftharpoons Pt(OH)(H_2O)_3{}^+ + (n-2)H_2O \qquad (3)$$

it has been argued[2] that it occurs in a range similar to that

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of reaction 3 (i.e., addition of sufficient acid to dissolve $Pt(OH)_2 \cdot nH_2O$ gives $Pt(H_2O)_4^{2+}$). The curves could equally well be explained if $Pt(OH)(H_2O)_3^+$ were the species present at pH 0–3.

On the other hand, it would require a very pronounced ligand effect to make $Pt(H_2O)_4^{2+}$ so much stronger an acid than *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ ($pK_a = 5.6$ at 20 °C).[12] As well, a protonation reaction need not necessarily cause a large change in chemical shift (e.g., at 10 °C, *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ has δ_{Pt} −1603; cf. *cis*-$Pt(NH_3)_2(OH)(H_2O)^+$, δ_{Pt} −1601).[13] At high acid concentrations, $HClO_4$ may have a very different effect from $NaClO_4$ on the structure of solvent water, which may affect ion-pairing interactions. It would therefore be dangerous to attribute the shift shown in Figure 1 just to reaction 2, and we will continue to refer to the solution in the pH range 0–3 as containing $Pt(H_2O)_4^{2+}$ (I). Little of the following discussion of results would be materially altered if the species present were actually $Pt(OH)(H_2O)_3^+$.

Addition of Alkali to Solutions of $[Pt(H_2O)_4](ClO_4)_2$. A 0.2 M solution of $[Pt(H_2O)_4](ClO_4)_2$ in perchloric acid at pH 0.5 gave a sharp peak (width at half-height 3 Hz) at 36 ppm. When the pH was raised to 1.5 by addition of 1 M NaOH solution, the signal shifted 3 ppm to higher shielding and broadened to width 9 Hz. At pH 2.5, the verge of hydroxide precipitation for a concentrated solution, the peak shifted a further −6 ppm and the width increased to 19 Hz. The shift on alkali addition is in the opposite direction to the shift when $HClO_4$ is added. The broadening may be caused by incomplete averaging of signals for species with different degrees of protonation, with possibly some contribution from formation of short-lived aggregates of $Pt(OH)_2(H_2O)_2$ molecules.

Solutions of $Pt(OH)_2 \cdot nH_2O$ in Alkali. Elding[2] reported that dilute (~10^{-2} M) solutions of I precipitated a white hydroxide on addition of alkali, which was insoluble over the pH range 4–10 but dissolved in acid or alkali. We have found that the precipitate, initially white, darkens if allowed to stand in contact with the mother liquor for more than 1 h, with decomposition faster when this liquor was more alkaline (e.g., faster at pH 9.7 than at 4.5). As Elding reported,[2] most of the solid (if freshly precipitated) redissolved in 1 M NaOH solution to give a colorless solution (although traces of undissolved solid usually remained).

Freshly prepared solutions, over the platinum concentration range 0.05–0.25 M at pH 14, gave only one ^{195}Pt signal, at −165 ppm, assigned to $Pt(OH)_4^{2-}$. Solutions with platinum concentrations greater than 0.05 M slowly deposited platinum metal, with the rate of deposition increasing with concentration (deposition commenced within 0.5 h for a 0.2 M solution). Solutions less concentrated than 0.02 M appeared to be stable indefinitely.

The ^{195}Pt spectrum of a concentrated solution after some platinum metal had deposited showed, in addition to the peak due to $Pt(OH)_4^{2-}$, a weak peak at 3270 ppm. A solid sample of $K_2Pt(OH)_6$[10] was dissolved in 1 M KOH solution. Its ^{195}Pt spectrum in 1 M KOH showed one sharp singlet at 3290 ppm. This shows that disproportionation reaction 4 is occurring in

$$2Pt(OH)_4^{2-} \rightarrow Pt\downarrow + Pt(OH)_6^{2-} + 2OH^- \quad (4)$$

the alkaline solution of $Pt(OH)_4^{2-}$. The concentration dependence noted above may indicate that disproportionation occurs via hydroxo-bridged species, which are well-known for ammine complexes.[13]

Reactions of Solutions of Platinum(II) Compounds with Hydrogen Peroxide. When 1 mL of 30% H_2O_2 solution was added to 2 mL of 0.2 M $Pt(OH)_4^{2-}$ at pH 14, and the solution was allowed to stand for 15 min at 25 °C, the peak at −165 ppm completely disappeared from the ^{195}Pt spectrum, to be replaced by a strong peak due to $Pt(OH)_6^{2-}$ at 3270 ppm (reaction 5).

$$Pt(OH)_4^{2-} + H_2O_2 \rightarrow Pt(OH)_6^{2-} \quad (5)$$

When 1 mL of a 30% H_2O_2 solution was added to 3 mL of a 0.2 M $[Pt(H_2O)_4](ClO_4)_2$ solution in 1 M $HClO_4$, little reaction occurred over several hours, but when the mixture was heated at 70 °C for 10 min, effervescence occurred and a bright orange solid precipitated. The ^{195}Pt spectrum of the supernatant liquid showed a weak peak at 3274 ppm ($Pt(OH)_6^{2-}$). The solid after drying was analyzed as $PtO_2 . 3H_2O$. This solid is quite different from $H_2Pt(OH)_6$, obtained by acidification of $Pt(OH)_6^{2-}$,[10,11] which is monomeric. The solid dissolves in 1 M NaOH solution to give a solution that shows a singlet at 3568 ppm, much less shielded than for $Pt(OH)_6^{2-}$. Species with four-membered $Pt(OH)_2Pt$ rings usually give peaks shifted in this direction from monomeric analogues,[13,14] so that this species may be $(HO)_4Pt(\mu\text{-}OH)_2Pt(OH)_4^{2-}$. This suggests that the orange solid may contain Pt–OH–Pt bridges.

Mixed Chloro–Aqua Complexes, $PtCl_n(H_2O)_{4-n}^{(2-n)+}$. Of the series $PtCl_n(H_2O)_{4-n}^{(2-n)+}$, ^{195}Pt chemical shifts have been previously reported for $PtCl_4^{2-}$,[15] $PtCl_3(H_2O)^-$ (in equilibrium with $PtCl_4^{2-}$ in aqueous solution),[16] and *trans*-$PtCl_2(H_2O)_2$.[7] Our values for the chemical shifts of these species (Table I) are in agreement with those in the literature.

The kinetics of reaction of I with chloride have been well established.[3,4] Because the trans effect of chloride is greater than that of water, $PtCl(H_2O)_3^+$ reacts relatively quickly with chloride to give *trans*-$PtCl_2(H_2O)_2$. This reaction is much faster than the initial reaction of I to give $PtCl(H_2O)_3^+$, or subsequent reactions of *trans*-$PtCl_2(H_2O)_2$ to $PtCl_3(H_2O)^-$ and $PtCl_4^{2-}$, and much faster than formation of *cis*-$PtCl_2(H_2O)_2$. *trans*-$PtCl_2(H_2O)_2$ is therefore the dominant species in solution when moderate amounts of chloride are added to a solution of I, and the mixture is allowed to stand for 1 h. The ^{195}Pt spectrum of *trans*-$PtCl_2(H_2O)_2$ has been previously run with use of such a solution.[7]

Solid sodium chloride was added to a 0.36 M solution of $[Pt(H_2O)_4](ClO_4)_2$ in 1 M $HClO_4$, to bring chloride concentration to 0.22 M. These concentrations are higher than those used by Elding.[7] Ten minutes after the addition, an intense peak due to I was still present at 25 ppm, with a moderately intense peak at −644 ppm due to *trans*-$PtCl_2(H_2O)_2$, and a much weaker peak at −350 ppm, which was assigned to $PtCl(H_2O)_3^+$. After 1 h, the peak due to *trans*-$PtCl_2(H_2O)_2$ had grown, but another weak peak was observed at −811 ppm, assigned to *cis*-$PtCl_2(H_2O)_2$.

In making these assignments, the general principles were applied that have been established for series such as $PtCl_{4-n}Br_n^{2-}$:[17] (a) successive substitution cause shift changes in the same direction; (b) differences in shift for geometric isomers are much less than differences when numbers of substituents are changed.

Nitrato Complexes. When sufficient sodium nitrate was added to a 0.2 M solution of $[Pt(H_2O)_4](ClO_4)_2$ in 1 M $HClO_4$ to bring nitrate ion concentration to 1.0–1.5 M, a new peak appeared in the ^{195}Pt NMR spectrum to higher shielding than that due to I, which was assigned to a mono(nitrato) complex. From this spectrum alone, it is not possible to determine

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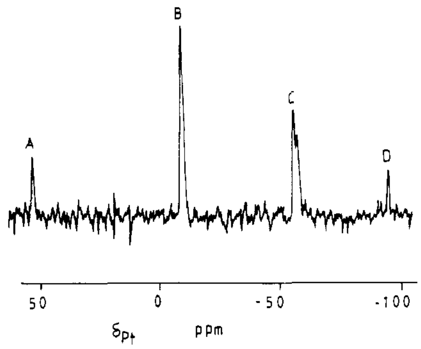

Figure 2. ^{195}Pt NMR spectrum (21.4 MHz) of an aqueous solution containing all of the species $Pt(ONO_2)_n(H_2O)_{4-n}{}^{(2-n)+}$ ($n = 0$ (A), 1 (B), 2 (C), 3 (D)). The spectrum was run on the double-precision mode with 8K points, width 10 KHz, 70° tilt, 0.5 s between pulses, 5000 scans.

whether nitrate is unidentate or bidentate. From ^{195}Pt and ^{15}N NMR spectra of the corresponding complex formed from *cis*-$Pt(^{15}NH_3)_2(H_2O)_2{}^{2+}$ and nitrate, we have shown that nitrate is unidentate, giving *cis*-$Pt(^{15}NH_3)_2(ONO_2)(H_2O)^+$.[8] By analogy, the complex formed from I is assigned as $Pt(ONO_2)(H_2O)_3{}^+$, with nitrate unidentate.

Spectra were run, with several seconds left between pulses to allow ^{195}Pt nuclei to relax completely, and then integrated. The equilibrium constant for formation of this complex (ignoring the concentration of water) was estimated as 0.25 ± 0.05 mol^{-1} L (cf. 0.17 mol^{-1} L for the ammine analogue[8]). Formation of a palladium analogue, $Pd(ONO_2)(H_2O)_3{}^+$, has been deduced from electronic spectra, with the equilibrium constant estimated as 1.2 ± 0.4 mol^{-1} L.[18]

Addition of more sodium nitrate, to bring nitrate concentration to 2–5 M, caused two new peaks, just resolved from one another, to appear in the ^{195}Pt spectrum, to still higher shielding. The relative heights of these two peaks changed little over several successive additions of nitrate. The two peaks were therefore assigned to *cis*- and *trans*-$Pt(ONO_2)_2(H_2O)_2$. There is no obvious basis for assigning each of the peaks to a particular isomer.

With nitrate concentration increased to 6 M, a fourth peak appeared to higher shielding than any of those previously detected. It was assigned to $Pt(ONO_2)_3(H_2O)^-$. Peaks due to I and the four nitrato complexes were present in the one spectrum (with that due to $Pt(ONO_2)(H_2O)_3{}^+$ dominant) (Figure 2).

The ^{195}Pt chemical shift for each species shows a relatively small dependence on sodium nitrate concentration. The values reported in Table I are at the lowest nitrate ion concentration for which the species could be detected.

In view of the dependence of δ_{Pt} for I on the $HClO_4$ concentration, and following the suggestion of a reviewer, we carried out an experiment to determine the effect of added perchloric acid on the NMR spectra of the nitrato complexes. To a solution 0.13 M in I and 0.33 M in free $HClO_4$ was added 0.66 g of solid $NaNO_3$. After standing, the solution showed ^{195}Pt peaks due to I (39.0 ppm), $Pt(ONO_2)(H_2O)_3{}^+$ (−21.7 ppm), and the isomers of $Pt(ONO_2)_2(H_2O)_2$ (−66.0, −67.4 ppm). After addition of concentrated $HClO_4$ solution to bring the concentration of free $HClO_4$ to 3.30 M, all of these peaks shifted to lower shielding—I to 76.4 ppm, the mono(nitrato) complex to 11.6 ppm, and the bis(nitrato) complexes to −40.6 and −40.8 ppm (almost coincident). The shift was larger for the less substituted complexes. Again, there was no indication of any perchlorate coordination.

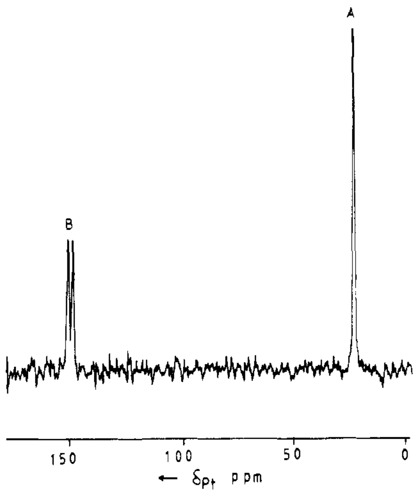

Figure 3. ^{195}Pt NMR spectrum (21.4 MHz) of a solution containing $Pt(H_2O)_4{}^{2+}$ (A) and $Pt(OPO_3H_2)(H_2O)_3{}^+$ (B). The spectrum was run on the double-precision mode with 8K points, width 10 KHz, 70° tilt, 0.5 s between pulses, 3100 scans.

Sulfato Complexes. Addition of sodium sulfate to a 0.2 M solution of $[Pt(H_2O)_4](ClO_4)_2$ in 1 M $HClO_4$, to bring sulfate concentration to 0.3–0.7 M, caused a new ^{195}Pt resonance to appear, to lower shielding than that due to I, which was assigned to a mono(sulfato) complex. Sulfate is unidentate in the corresponding ammine complex,[8] so this complex is assigned as $Pt(OSO_3)(H_2O)_3$. The formation constant (ignoring concentration of water) from integration was 0.58 ± 0.05 mol^{-1} L, a little lower than for the ammine complex (1.7 ± 0.2 mol^{-1} L). The palladium analogue, $Pd(OSO_3)(H_2O)_3$, has been detected by visible–UV spectroscopy.[18]

When sulfate concentration was increased beyond 0.75 M, two new peaks appeared to lower shielding, whose relative intensities showed little dependence on further additions of sulfate. These were assigned to *cis*- and *trans*-$Pt(OSO_3)_2(H_2O)_2{}^{2-}$. The difference in chemical shift between the isomers (31 ppm) is much greater than for nitrate (2 ppm).

Phosphato Complexes. When NaH_2PO_4 was added to a 0.2 M solution of $[Pt(H_2O)_4](ClO_4)_2$ in 1 M $HClO_4$ solution, to bring the sodium ion concentration to 1–2 M, no peaks other than that due to I appeared in the ^{195}Pt NMR spectrum. This is presumably because all phosphate is fully protonated under these conditions. When the pH was raised above 1.5 by addition of NaOH solution, an additional resonance appeared, but peaks were broad. When the pH was decreased to <1 by addition of $HClO_4$, the peaks sharpened, revealing that the new resonance was a doublet (Figure 3). The ^{31}P NMR spectrum showed a singlet with "satellites" +8.6 ppm from the signal due to H_3PO_4 ($^2J_{Pt-O-P} = 36$ Hz). This corresponds to the doublet separation in the ^{195}Pt spectrum. This complex is assigned as $Pt(OPO_3H_2)(H_2O)_3{}^+$, by analogy with the ammine complex, *cis*-$Pt(NH_3)_2(OPO_3H_2)(H_2O)^+$.[8] $^2J_{Pt-O-P}$ in the latter complex, 26.8 Hz, is smaller than in the triaqua complex, due to the high trans influence of ammine relative to aqua ligands.[19]

Complexes with more than one coordinated phosphate were observed as follows: solid $NaH_2PO_4 \cdot 2H_2O$ was added, the pH was increased to 2.0–2.5, the solution was allowed to stand for 1–2 h to allow complex formation and then acidified to pH <1, and ^{195}Pt spectra were run. Peaks attributed to bis- (cis and trans), tris-, and (in solutions with total phosphate concentration ~10 M) tetrakis(phosphato) complexes were observed. Pt–O–P coupling was not resolved for any of these

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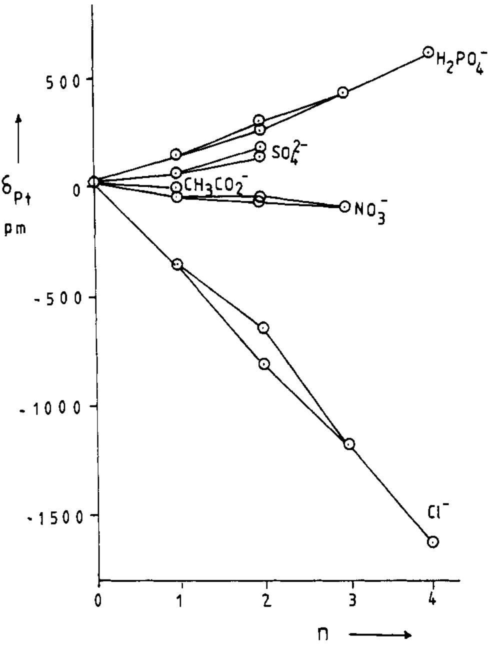

Figure 4. Dependence of ^{195}Pt chemical shift of $Pt(A)_n(H_2O)_{4-n}^{(2-mn)+}$ on *n* (A^{m-} = Cl^-, ONO_2^-, OSO_3^{2-}, $OPO_3H_2^-$, $O_2CCH_3^-$).

species. ^{31}P peaks were obscured by the very intense H_3PO_4 resonance.

Although none of these complexes is formed at pH 1.5, solutions at pH 1 showing all the peaks do not change appreciably over several weeks.

A 0.2 M solution of I with 1 M phosphate allowed to stand at pH >1.5 began, after several hours, to deposit a black solid. After 24 h, the ^{195}Pt NMR spectrum showed no ^{195}Pt peaks. The solid dissolved in warmed 1 M HCl to give a red solution, whose ^{195}Pt spectrum showed only a peak due to $PtCl_4^{2-}$, and whose ^{31}P spectrum showed a peak due to H_3PO_4. The solid appears to be a phosphato-platinum compound, predominantly Pt(II) but presumably contains sufficient higher oxidation state material to cause the dark color (cf. ammine complexes).[8,20]

Reaction with Acetate. As with phosphate, no discernible reaction occurs between I and acetate at pH less than 1.5. When the pH of a 0.2 M solution of $[Pt(H_2O)_4](ClO_4)_2$ and 1.0–2.5 M sodium acetate was raised to 2 and the solution allowed to stand for 2 h, an additional resonance appeared. Peaks were broad at this pH but sharpened when the solution was reacidified, to pH below 1. The new peak, to higher shielding than that due to I, was assigned to $Pt(O_2CCH_3)(H_2O)_3^+$, analogous to the case for *cis*-$Pt(NH_3)_2(O_2CCH_3)(H_2O)^+$.[8] No additional peaks were observed with total acetate concentration up to 8 M.

When these solutions were allowed to stand in the presence of air, intense blue colors developed. No insoluble solids deposited.

Discussion

^{195}Pt Chemical Shifts. The chemical shift for $Pt(OH)_6^{2-}$ is reported here for the first time, 3290 ppm. The deshielding relative to the shift for $PtCl_6^{2-}$ is expected. Only PtF_6^{2-} (7326 ppm)[21] has been reported at higher shielding. In the absence of "small ring" effects[13] the ^{195}Pt chemical shift depends mainly on the donor atoms. Donors that bond very covalently (e.g., CH_3^-, CN^-) cause shifts to higher shielding. Heavy donor atoms (e.g., I^-) also cause shielding.[22] Since water does not form strong covalent bonds, and oxygen is a light donor atom, it is not surprising that platinum bound to water is less shielded than when it is bound to most other ligands in corresponding complexes. Pregosin[23] has previously noted that, in the series $PtCl_3L^-$, shielding decreases in the order L = $P(CH_3)_3$ > $N(CH_3)_3$ > H_2O. Although the ^{195}Pt chemical shift for I has been previously reported,[6,7] there has to date been no comment on its position in the scale. I and the complexes with O-donor ligands described here have a platinum nucleus less shielded than for any other reported platinum(II) complexes (the distinction of being least shielded is held by $Pt(OPO_3H_2)_4^{2-}$, at 602 ppm). The only complexes likely to have appreciably lower shielding would be fluoro complexes such as PtF_4^{2-}, by analogy with the platinum(IV) chemical shift series.

Figure 4 shows the variation in δ_{Pt} with *n*, the number of anionic ligands, A^{m-}, in the series $Pt(A)_n(H_2O)_{4-n}^{(2-mn)+}$. Of the ligands examined, chloride has the largest effect, a shift to higher shielding. Some of the O-donor ligands (nitrate, acetate) also cause a shift to higher shielding, while others (sulfate, dihydrogen phosphate) cause a shift to lower shielding. The same ligands cause shifts in the same directions for the derivatives of *cis*-$Pt(^{15}NH_3)_2(H_2O)_2^{2+}$.[8] There is no obvious reason for this difference. Perhaps it is significant that ions which have tetrahedral geometry cause deshielding and those which have trigonal geometry about the central atom cause shielding.

If the shifts for cis and trans isomers are averaged, the variation of δ_{Pt} with *n* is close to linear for each series for A^{m-} = Cl^-, NO_3^-, but curvature is evident for sulfate and phosphate, with $\Delta\delta$ increasing slightly as *n* increases (cf. series such as $PtCl_{4-n}Br_n^{2-}$ and $PtCl_{6-n}Br_n^{2-}$ [16]).

Registry No. I, 83420-61-5; $Pt(OH)_4^{2-}$, 91781-18-9; $Pt(OH)_6^{2-}$, 19559-03-6; $(HO)_4Pt(\mu\text{-}OH)_2Pt(OH)_4^{2-}$, 91781-19-0; $Pt(ONO_2)(H_2O)_3^+$, 91781-20-3; *cis*-$Pt(ONO_2)_2(H_2O)_2$, 91781-21-4; *trans*-$Pt(ONO_2)_2(H_2O)_2$, 91840-30-1; $Pt(ONO_2)_3(H_2O)^-$, 91781-22-5; $Pt(OSO_3)(H_2O)_3$, 91781-23-6; *cis*-$Pt(OSO_3)_2(H_2O)_2^{2-}$, 91781-24-7; *trans*-$Pt(OSO_3)_2(H_2O)_2^{2-}$, 91840-31-2; $Pt(OPO_3H_2)(H_2O)_3^+$, 91781-25-8; *cis*-$Pt(OPO_3H_2)_2(H_2O)_2$, 91781-26-9; *trans*-$Pt(OPO_3H_2)_2(H_2O)_2$, 91840-32-3; $Pt(OPO_3H_2)_3(H_2O)^-$, 91781-27-0; $Pt(OPO_3H_2)_4^{2-}$, 91781-28-1; $Pt(O_2CCH_3)(H_2O)_3^+$, 91781-29-2; $PtCl(H_2O)_3^+$, 30210-69-6; *cis*-$PtCl_2(H_2O)_2$, 15489-35-7; *trans*-$PtCl_2(H_2O)_2$, 13876-96-5; $PtCl_3(H_2O)^-$, 15489-34-6; $PtCl_4^{2-}$, 13965-91-8; PtO_2, 1314-15-4; ^{195}Pt, 14191-88-9.

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