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means that very large volumes of the zeolite would have to be used. In principle, it should be possible to form a complex in every large cavity of the zeolite.

Acknowledgment. We are grateful to Dr A. E. Martell for bringing to our attention the mixed-ligand bipyridine–terpyridine complex of cobalt. The Q-band EPR spectrum was kindly obtained by Dr. W. S. Millman at the University of Wisconsin–Milwaukee. This work was supported by the U.S. Army Research Office.

Registry No. [Co^{II}(terpy)$_2$]$^{2+}$, 18308-16-2; [Co^{II}(bpy)(terpy)]$^{2+}$, 52225-38-4; [Co^{III}(bpy)(terpy)O$_2^-$]$^{2+}$, 91743-35-0.

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Reactions of Platinum(II) Aqua Complexes. 1. Multinuclear (^{195}Pt, ^{15}N, and ^{31}P) NMR Study of Reactions between the *cis*-Diamminediaquaplatinum(II) Cation and the Oxygen-Donor Ligands Hydroxide, Perchlorate, Nitrate, Sulfate, Phosphate, and Acetate[1]

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Reactions in aqueous solution between *cis*-[Pt(^{15}NH$_3$)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ and anions A^{m-} (ClO$_4^-$, OH$^-$, NO$_3^-$, SO$_4^{2-}$, H$_2$PO$_4^-$, CH$_3$CO$_2^-$) have been studied with use of ^{195}Pt, ^{15}N, and, for phosphate, ^{31}P NMR. The monohydroxo-bridged complex (Pt(NH$_3$)$_2$(H$_2$O))$_2$(μ-OH)$^{3+}$ has been obtained in solution by reaction of [Pt(NH$_3$)$_2$(μ-OH)]$_n^{n+}$ with acid or as an intermediate in the formation of these oligomers from *cis*-Pt(NH$_3$)$_2$(OH)(H$_2$O)$^+$. Perchlorate does not coordinate. Nitrate and sulfate each gives a complex *cis*-Pt(NH$_3$)$_2$(A)(H$_2$O)$^{(2-m)+}$, with A^{m-} unidentate. In acidic solution (pH 1.5), phosphate gives only *cis*-Pt(NH$_3$)$_2$(OPO$_3$H$_2$)(H$_2$O)$^+$. When deprotonated, this complex is in equilibrium with (Pt(NH$_3$)$_2$)$_2$(μ-OH)(μ-PO$_4$H)$^+$ and other complexes containing bridging phosphate. Reaction with oxygen gives blue solids and solutions. Analogous phosphate complexes are formed with methylamine and ethylenediamine, although blue solutions with methylamine are obtained only after prolonged exposure to light. In solution, acetate gives *cis*-Pt(NH$_3$)$_2$(O$_2$CCH$_3$)(H$_2$O)$^+$, and Pt(NH$_3$)$_2$(O$_2$CCH$_3$)$_2$, with smaller amounts of (Pt(NH$_3$)$_2$)$_2$(μ-OH)(μ-O$_2$CCH$_3$)$^{2+}$. With perchlorate, a solid [Pt(NH$_3$)$_2$(O$_2$CCH$_3$)]ClO$_4$·H$_2$O crystallizes, which probably contains bridging acetate. Solutions turn blue-black when heated, indicating that oligomers with mixed oxidation states of platinum form. Solid *cis*-Pt(NH$_3$)$_2$(O$_2$CCH$_3$)$_2$·2H$_2$O may be isolated. It is quite soluble in water.

Introduction

There has been considerable interest in platinum(II) amine complexes since the discovery that *cis*-Pt(NH$_3$)$_2$Cl$_2$ and a number of analogues possess antitumor activity.[2] Many syntheses, including the now standard Dhara method for preparing the compounds *cis*-Pt(NH$_2$R)$_2$Cl$_2$,[3] use the aqua complexes *cis*-Pt(NH$_2$R)$_2$(H$_2$O)$_2^{2+}$ as intermediates. Despite this, relatively little is known of the solution chemistry of the aqua complexes, including the extent of reaction with the weakly coordinating counterions usually present (reaction 1).

$$cis\text{-Pt(NH}_2\text{R)}_2\text{(H}_2\text{O)}_2^{2+} + A^{m-} \rightleftharpoons \text{Pt(NH}_2\text{R)}_2\text{(A)(H}_2\text{O)}^{(2-m)+} + \text{H}_2\text{O} \quad (1)$$

When ^{15}N-substituted ammonia is used, ^{195}Pt and ^{15}N NMR can be very useful in investigating reactions of *cis*-Pt(NH$_3$)$_2$(H$_2$O)$_2^{2+}$.[4-7] In this work, NMR spectroscopy with these nuclei has been used to study reactions 1.

We have previously shown[8] that a number of the complexes *cis*-Pt(NH$_2$R)$_2$(H$_2$O)$_2^{2+}$ rapidly give blue solutions and solids when mixed with phosphate and exposed to air. We have used ^{31}P NMR in conjunction with ^{195}Pt and ^{15}N NMR to examine these solutions. While this paper was in preparation, a report appeared giving some preliminary ^{195}Pt and ^{31}P data on similar solutions, but no attempt was made to assign the resonances to specific complexes.[9]

Experimental Section

Instruments and Techniques. NMR spectra at 10.1 MHz (^{15}N), 21.4 MHz (^{195}Pt), 25 MHz (^{13}C), and 40.3 MHz (^{31}P) were obtained with a JEOL FX-100 instrument, with a tunable 10-mm multinuclear probe, at 28 °C. ^{15}N spectra were run at 2000 Hz width, typically by using 2000 scans, with 3 s between 10-μs pulses (22° tilt). Shifts are relative to the ^{15}NH$_4^+$ signal from 5 M ^{15}NH$_4$^{15}NO$_3$ in 2 M HNO$_3$ contained in a coaxial capillary.[10] ^{195}Pt spectra were obtained typically with spectrum width 20 or 10 KHz, 1000–3000 scans, total delay 0.3–0.5 s between 20-μs pulses (70 tilt), and a separate aqueous solution of Na$_2$PtCl$_6$ as reference.[11] ^{31}P spectra were obtained with use of 10-KHz scans, 100 10-μs pulses at 1-s intervals (27° tilt). Spectra were initially referenced relative to free phosphate in the solutions and then adjusted relative to external 85% H$_3$PO$_4$ following calibration of the shift of free phosphate in solution as a function of pH. Below pH 3, there was no significant difference between the shifts. All these

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spectra were run with use of external ^{7}Li lock, initially with 8K data points on the double-precision mode. Where higher resolution was required, 16K points were sometimes used. All shifts are positive to lower shielding.

For acetate complexes, ^{13}C spectra were obtained with internal deuterium lock, with use of a coaxial capillary of D_2O. Spectra were run with spectrum width 8000 Hz, 16K data points, and double-precision mode, with 18 000 scans, 3 s apart at 10-μs pulse width (35° tilt). Shifts are relative to external tetramethylsilane, with the shift for internal dioxane in water taken as 67.73 ppm.[12] ^{1}H NMR spectra were run on a JEOL PS-100 (CW) instrument and are referenced to sodium 3-(trimethylsilyl)propanesulfonate (TSS).

IR spectra were recorded on a Perkin-Elmer 283b spectrometer with Nujol and hexachlorobutadiene mulls and KBr disks.

Microanalyses were carried out by J. Kent and P. Nobbs in this department and by the Australian Microanalytical Service, Melbourne, Australia.

pH was measured with Merck narrow-range indicator strips, checked against glass electrode measurements.

Starting Materials. $^{15}NH_4Cl$ (99.0% ^{15}N) was supplied by Novachem Ltd., Melbourne, Australia. *cis*-$Pt(NH_3)_2Cl_2$ (whether ^{14}N or ^{15}N ammine) was prepared by Broomhead's modification of the Dhara synthesis,[5] and diaminoethane and methylamine analogues were prepared by similar procedures. Solutions of *cis*-$Pt(NH_2R)_2(H_2O)_2{}^{2+}$ with perchlorate, nitrate, or sulfate as counterions were prepared as follows: Approximately 0.5 g of solid *cis*-$Pt(NH_2R)_2Cl_2$ was suspended in 50 mL of water, and a standard solution of the appropriate silver salt was added by buret until 1.98 mol of silver salt/mol of complex had been added. The mixture was heated at 60 °C, with stirring, and protected from light, for 4 h, and then stirred at room temperature for 16 h. Silver chloride was filtered off and the filtrate concentrated on a rotary evaporator until the volume was less than 10 mL. It was then transferred to a 10-mL volumetric flask and made up to the mark. Since this procedure is nearly quantitative in yield, concentration sufficiently accurate for most purposes may be calculated from the quantity of *cis*-$Pt(NH_2R)_2Cl_2$ used.

Solid *cis*-$Pt(NH_3)_2(NO_3)_2$ was obtained by evaporating a solution of *cis*-$[Pt(NH_3)_2(H_2O)_2](NO_3)_2$, protected from light, to dryness on a rotary evaporator.

***cis*-$Pt(NH_3)_2(SO_4)(H_2O)$.** Evaporation of an aqueous solution of *cis*-$[Pt(NH_3)_2(H_2O)_2]SO_4$ to dryness under a stream of nitrogen at room temperature yielded a solid that was analyzed as $Pt(NH_3)_2(SO_4)(H_2O)$. Initially colorless, it rapidly assumed a grey appearance, even when protected as much as possible from light and air. Examination under a microscope revealed that this was due to a thin surface coating of a dark blue material. Anal. Calcd for $H_8N_2O_5PtS$: H, 2.4; N, 8.2; Pt 56.8; S, 9.3. Found: H, 2.4; N, 8.2; Pt, 56.8; S, 9.0.

The solid slowly dissolves in cold water, more rapidly with warming, to give a colorless solution. Heating a sample at 110 °C in a drying pistol over silica gel causes some loss of water over several hours. This is, however, accompanied by darkening of the sample.

Small amounts of this product also slowly deposit from aqueous solutions of *cis*-$[Pt(NH_3)_2(H_2O)_2](ClO_4)_2$ to which large amounts of sodium sulfate have been added.

$Pt(NH_3)_2(SO_4)$. The anhydrous compound was most readily prepared by evaporation of a solution of *cis*-$[Pt(NH_3)_2(H_2O)_2]SO_4$ to dryness on a boiling steam bath. Anal. Calcd for $H_6N_2O_4PtS$: H, 1.9; N, 8.6; S, 9.9. Found: H, 2.4; N, 8.6; S, 9.7.

This product is a cream white solid that shows no sign of surface discoloration. It does not dissolve in cold water and dissolves only slowly in boiling water. It may also be obtained in microcrystalline form by adding 2 molar equiv of $Na_2SO_4 \cdot 10H_2O$ to an aqueous solution of *cis*-$[Pt(NH_3)_2(H_2O)_2](ClO_4)_2$ and then concentrating the solution by boiling on a hot plate until the product crystallized.

Temperature determines which of the two solids is obtained. Evaporation of a solution of *cis*-$[Pt(NH_3)_2(H_2O)_2]SO_4$ in a rotary evaporator over warm water gave a mixture of $Pt(NH_3)_2(SO_4)$ and $Pt(NH_3)_2(SO_4)(H_2O)$.

"White" $Pt(NH_3)_2(PO_4H) \cdot 0.5H_2O$. *cis*-$Pt(NH_3)_2(NO_3)_2$ (0.1975 g, 0.559 mmol) was dissolved with warming in 7 mL of water. $NaH_2PO_4 \cdot 2H_2O$ (0.223 g, 1.43 mmol) in 1 mL of water was added, under nitrogen. pH was adjusted from its initial value, 3.5, to 2.5 with 1 M HNO_3 solution. The solution was allowed to stand overnight, during which time a grayish white solid deposited and the pH of the colorless solution had reduced to 2. This product was filtered off (0.038 g). After the filtrate had stood a further 24 h under nitrogen, a further 0.029 g of solid was filtered off. After 4 days' further standing, little additional solid deposited from the filtrate. NaOH solution (1 M) was added to increase the pH again to 3, after which a further 0.040 g of solid deposited. This had a slight blue tinge but gave an IR spectrum similar to those of the earlier fractions.

If similar procedures were carried out in air, the solids tended to be very pale blue, rather than gray-white. Anal. Calcd for $H_8N_2O_{4.5}PPt$: H, 2.7; N, 8.4; P, 9.2; Pt, 58.2. Found: H, 2.5; N, 8.5; P, 9.2; Pt, 58.5.

"Blue" $Pt(NH_3)_2(PO_4H) \cdot 0.5H_2O$. At pH 3–7, solutions prepared from *cis*-$Pt(NH_3)_2(H_2O)_2{}^{2+}$ and phosphate salts rapidly turned blue in air, and quantities of dark blue solid precipitated. With as much care as possible, under nitrogen, we were not able to isolate white solids at pH >3.

Relatively small quantities of blue solids slowly precipitate from solutions maintained near pH 4. The following procedure gave a larger quantity of a very dark blue-black sample.

KH_2PO_4 (0.24 g, 1.76 mmol) in 0.5 mL of water was added to a solution of *cis*-$Pt(NH_3)_2(NO_3)_2$ (0.623 g, 1.76 mmol) in 2 mL of water. The pH was immediately adjusted to 4 with 1 M KOH solution. The solution began to turn green-blue within 0.5 h and deep blue within 2 h. Small quantities of pale blue precipitate were removed by filtration, and the filtrate was evaporated to dryness in a stream of air. The resultant dark blue gum was triturated with acetone until it solidified. The acetone was decanted off, and the solid was washed thoroughly with water to remove soluble salts and then washed again with acetone, transferred to a glass sinter, and dried in air and then in a vacuum desiccator over silica gel. The product was insoluble in water but dissolved in concentrated HNO_3 to give a pale yellow solution and in concentrated KOH solution to give a brown solution. Anal. Calcd for $Pt(NH_3)_2(PO_4H) \cdot 0.5H_2O$, $H_8N_2O_{4.5}PPt$: H, 2.7; N, 8.4; P, 9.2. Found: H, 2.6; N, 8.2; P, 9.1.

$Pd(en)(PO_4H)$. A solution of $[Pd(en)(H_2O)_2](NO_3)_2$ was prepared from $Pd(en)Cl_2$ and silver nitrate as for the platinum analogues. To 2 mL of 0.4 M solution (0.80 mmol) was added 0.135 g of solid $NaH_2PO_4 \cdot 2H_2O$ (0.87 mmol). Precipitation of a yellow-brown solid began within a few minutes. After the mixture was allowed to stand overnight, the solid was filtered off, washed with cold water, and dried in a vacuum desiccator over silica gel. Yield was 90.3% (0.190 g). Anal. Calcd for $C_2H_9N_2O_4PPd$: C, 9.1; H, 3.5; N, 10.7; P, 11.8; Pd, 40.7. Found: C, 8.8; H, 3.7; N, 10.7; P, 12.2; Pd, 41.2.

$[Pt(NH_3)_2(CH_3CO_2)](ClO_4) \cdot H_2O$. To 2 mL of 0.54 M *cis*-$[Pt(NH_3)_2(H_2O)_2](ClO_4)_2$ solution (1.08 mmol) was added 0.148 g of solid sodium acetate trihydrate (1.09 mmol). The pH of the pale yellow solution was initially 5. After 10 min, the solution turned deeper yellow, and bright yellow filamentous crystals deposited. The mixture was allowed to stand in a refrigerator overnight, after which the pH had decreased to 4. The solid was filtered off with use of a small Büchner funnel (*Caution*! perchlorate salt) and washed with 1 mL of cold water. The solid was air-dried and then dried in a vacuum desiccator over silica gel; yield 0.212 g (48.3%). It is only very sparingly soluble in cold water. It redissolves readily in hot water, but heating and concentrating these solutions cause formation of very dark blue-black solutions. Anal. Calcd for $C_2H_{11}ClN_2O_7Pt$: C, 5.9; H, 2.7; N, 6.9. Found: C, 6.0; H, 2.5; N, 7.0.

***cis*-$Pt(NH_3)_2(O_2CCH_3)_2 \cdot 2H_2O$.** *cis*-$Pt(NH_3)_2Cl_2$ (1.00 g, 3.33 mmol) was ground finely with 1.00 g of silver acetate (6.00 mmol). Fifty milliliters of water was added to the solid. The mixture was stirred at 50 °C while protected from light and then stirred at room temperature for 22 h. Silver chloride was removed by filtration, the paper was washed twice with 5 mL of water, and the washings were combined with the filtrate. Nitrogen was blown over the solution in the dark until an oil was obtained. The oil was dissolved in methanol, the solution was filtered, and the volume was reduced to give a cream-colored solid, which was filtered off, washed with 1 mL of ethanol, and dried in a vacuum desiccator for 4 days over silica gel; yield 0.67 g, 52.5%. The surface of the solid slowly turns green on exposure to air and light. Anal. Calcd for $C_4H_{16}N_2O_6Pt$: C, 12.5; H, 4.2; N, 7.3; Pt, 50.9. Found: C, 12.2; H, 4.1; N, 7.3; Pt, 51.0.

Results

^{195}Pt and ^{15}N NMR data are given in Table I and ^{31}P data for phosphate complexes in Table II.

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Table I. ^{195}Pt and ^{15}N NMR Parameters

		$\delta_{^{15}N}{}^{c}$ ($J_{^{195}Pt-^{15}N}$)^{d}	
compd^{a}	$\delta_{Pt}{}^{b}$	trans H_2O	trans A^{m-}
$[Pt(NH_3)_2(H_2O)_2](ClO_4)_2$ (I)	−1583.7	−85.83 (390.6)	
$(Pt(NH_3)_2(H_2O))_2(\mu\text{-}OH)^{3+}$ (II)	−1546.8	−83.13 (396.5)	−81.83 (339.3)
$(Pt(NH_3)_2(OH))_2(\mu\text{-}OH)^{+}$	−1516.3		−73.98 (298)^{e} −82.15 (334)^{f}
$Pt(NH_3)_2(ONO_2)(H_2O)^{+}$ (III)	−1598.4	−85.47 (403.4)	−85.47 (377.8)
$Pt(NH_3)_2(OSO_3)(H_2O)$ (V)	−1550.0	−85.10 (395.5)	−86.80 (378.2)
$Pt(NH_3)_2(OPO_3H_2)(H_2O)^{+}$ (X)	−1502.1	−85.54 (392.6)	−86.46 (377.2)
$Pt(NH_3)_2(OPO_3H)(H_2O)$ (XI)	−1522	−85.8^{i}	−85.8^{j}
$(Pt(NH_3)_2)_2(\mu\text{-}OH)(\mu\text{-}PO_4H)^{+}$ (XIII)	−1480.6	...	−79.30 (342)^{f} −83.38 (366)^{g}
$Pt(NH_3)_2(O_2CCH_3)(H_2O)^{+}$ (XVII)	−1585.0	−87.19 (393.6)	−81.67 (348.1)^{h}
$Pt(NH_3)_2(O_2CCH_3)_2$ (XVIII)	−1581.5	...	−83.12 (349.1)^{h}
$(Pt(NH_3)_2)_2(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)^{2+}$ (XIX)	−1548.2	...	−77.36 (351.1)^{f} −83.01 (376.9)^{h}

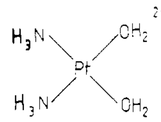
^{a} Data for ^{15}N-substituted compounds, in H_2O (~0.3 M). All compounds have cis-ammine ligands. ^{b} All values to lower shielding from aqueous Na_2PtCl_6. ^{c} All values to lower shielding from external $^{15}NH_4{}^{+}$. ^{d} Coupling constants in Hz, measured from ^{15}N spectra. ^{e} Trans to terminal hydroxide. ^{f} Trans to bridging hydroxide. ^{g} Trans to phosphate. ^{h} Trans to acetate. ^{i} Peaks coincident with peak from I; Pt-N coupling not clearly resolved.

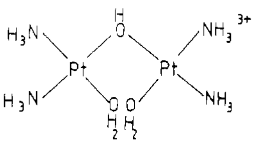
Table II. ^{31}P NMR Parameters for Phosphate Complexes

	$\delta_{P}{}^{b}$ (J_{Pt-P})^{c}		
compd type^{a}	NH_2R = NH_3	NH_2R = NH_2CH_3	NH_2R = 1/2 en
$Pt(NH_2R)_2(PO_4H_2)(H_2O)^{+}$ (X)	5.75 (26.8)	5.93 (24.4)	6.02 (29.6)
$Pt(NH_2R)_2(PO_4H)(H_2O)$ (XI)	7.90	8.27	7.50
$(Pt(NH_2R)_2(H_2O))_2(PO_4H)^{2+}$ (XII)^{d}	5.42	5.48	5.66
$(Pt(NH_2R)_2)_2(\mu\text{-}OH)(\mu\text{-}PO_4H)^{+}$ (XIII)	7.91	8.27	*e*

^{a} Amine ligands cis for all compounds. ^{b} All values to lower shielding from external 85% H_3PO_4. ^{c} When coupling resolved; in H_2O, with units of Hz. ^{d} Assignment tentative. ^{e} No definite assignment.

Solutions of *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](ClO_4)_2$. As previously reported,[4-6] the ^{1}H-decoupled ^{195}Pt NMR spectrum (^{195}Pt, $I = 1/2$, 34% abundance) of a solution of *cis*-$Pt(^{15}NH_3)_2(H_2O)_2{}^{2+}$ (I) shows a 1:2:1 triplet (Figure 1b) due to coupling between ^{195}Pt and two equivalent ^{15}N nuclei (I = 1/2) ($^{1}J_{^{195}Pt-^{15}N}$ = 390.6 Hz). We have run all spectra in H_2O, rather than D_2O, to avoid any possibility of N-deuteration. The ^{1}H-coupled spectrum (Figure 1a) shows a triplet of septets, due to ^{195}Pt–N–^{1}H coupling (70.8 Hz). That the relative simplicity of the ^{1}H-decoupled spectrum is obtained at some cost is evident from a comparison of line widths in Figure 1. The 10-fold increase in line width and the peak asymmetry in the decoupled spectrum can only be due to differential heating across the sample by the decoupling irradiation—the so-called "skin effect".[13] The effect becomes more pronounced as total electrolyte concentration increases and would be more significant at higher field strengths.


I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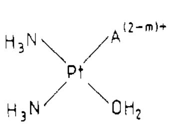
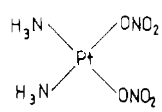



IV

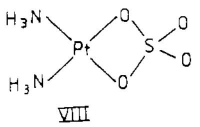
III $A^{m-} = ONO_2{}^{-}$

V $OSO_3{}^{2-}$

X $OPO_3H_2{}^{-}$

XI OPO_3H^{2-}

XVII $O_2CCH_3{}^{-}$


VIII

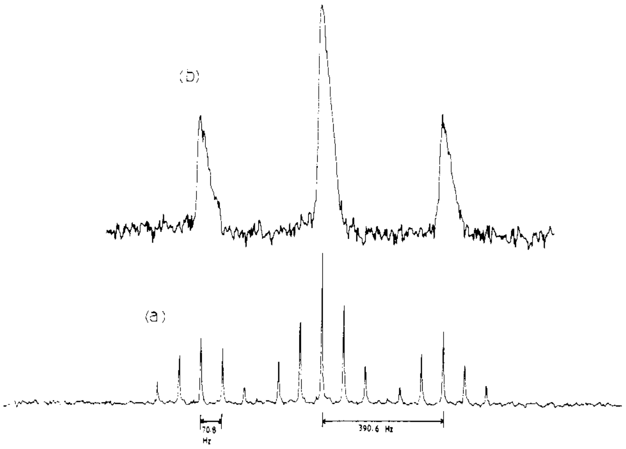


Figure 1. ^{195}Pt NMR spectra of 0.57 M *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](ClO_4)_2$ in H_2O: (a) without ^{1}H decoupling; (b) with ^{1}H decoupling. Conditions were as defined in the Experimental Section, except that there were only 200 scans and 16K data points at 20 KHz width.

As previously reported,[5,7] the ^{1}H-decoupled ^{15}N NMR spectrum of I shows a singlet with "satellites" from ^{195}Pt–^{15}N coupling, with each satellite one-fourth the intensity of the center peak. Even when electrolyte concentration is high, the lines remain sharp (~1 Hz wide). The differential heating effect is much less important here than for ^{195}Pt, because the temperature dependence of the ^{15}N chemical shifts is much less than for ^{195}Pt. ^{195}Pt–^{15}N coupling constants are therefore usually obtained more accurately from ^{15}N spectra (±1 Hz) than from ^{1}H-decoupled ^{195}Pt spectra (±5 Hz).

The ^{1}H-coupled spectrum shows a 1:3:3:1 quartet, with "satellite" quartets ($^{1}J_{^{15}N-^{1}H}$ = 73.3 Hz in agreement with the value obtained by Alei et al.[7]). $^{2}J_{^{15}N-Pt-^{15}N}$ must be small, since the spin system (for nonmagnetic Pt nuclei) is $A_3XX'A'_3$, which would give a more complex pattern if $|J_{X-X'}|$ were significant relative to $|J_{AX}|$.[14]

No new peaks due to perchlorato complexes were observed when large quantities of perchlorate salts were added to a solution of cis-$[Pt(^{15}NH_3)_2(H_2O)_2](ClO_4)_2$.

Hydroxo Complexes. When the pH of an aqueous solution of *cis*-$Pt(NH_3)_2(H_2O)_2{}^{2+}$ is increased to 7, the oligomers $[Pt(NH_3)_2(\mu\text{-}OH)]_n{}^{n+}$ form (n = 2, 3). They have been

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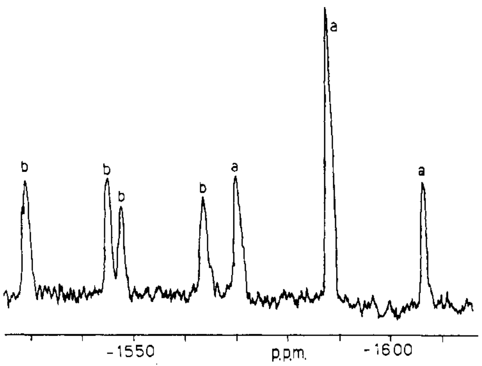

Figure 2. ^{195}Pt NMR spectrum of a solution containing *cis*-Pt($^{15}NH_3$)$_2$(H_2O)$_2^{2+}$ (I) (peaks labeled "a") and (Pt($^{15}NH_3$)$_2$-(H_2O))$_2$(μ-OH)$^{3+}$ (II) (peaks labeled "b") at pH 3.

characterized in solution by ^{195}Pt$^{4-6}$ and ^{15}N^{5} NMR and in the solid state by X-ray crystal structure determinations on salts of the dimer[15-17] and trimer.[18]

Broomhead et al.[5] reported that the oligomers reacted rapidly with dilute mineral acid (pH ~1) to give *cis*-Pt(NH_3)$_2$(H_2O)$_2^{2+}$ (I). We have found, however, that if the amount of $HClO_4$ added is limited, so that pH does not decrease below 2, a new compound is formed along with I, in comparable concentration. The ^1H-decoupled ^{195}Pt NMR spectrum of the ^{15}N-substituted compound shows a doublet of doublets (Figure 2) and the ^{15}N spectrum two singlets with satellites. The two ^{15}N nuclei are therefore nonequivalent. The ^{195}Pt–^{15}N coupling constants, 396.5 and 339.5 Hz, may be compared with those for $^{15}NH_3$ trans to H_2O in I (390.6 Hz) and trans to bridging hydroxide in [Pt($^{15}NH_3$)$_2$(μ-OH)]$_2^{2+}$ (342 Hz).[5] These data are consistent with structure II. At pH 3 and 25 °C, II is stable indefinitely but is converted to I when the solution is heated. No splitting of peaks due to ^{15}N–Pt–^{15}N coupling was observed.

When the pH of a solution of I was adjusted to 7 and the ^{195}Pt spectrum run as soon as possible, peaks due to [Pt($^{15}NH_3$)$_2$(μ-OH)]$_2^{2+}$ grew over several minutes; then, at concentrations greater than 0.05 M, peaks due to trimer also grew and eventually became dominant. A number of relatively weak transient peaks were also observed, which appeared and then disappeared during the first few minutes after pH adjustment. The species corresponding to most of these could not be identified, but weak peaks due to II were well-defined. It appears very likely that II is an intermediate in the formation of [Pt(NH_3)$_2$(μ-OH)]$_2^{2+}$ from Pt(NH_3)$_2$(OH)(H_2O)$^+$.

If the pH of a solution of *cis*-Pt($^{15}NH_3$)$_2$(H_2O)$_2^{2+}$ (I) is quickly increased to 12.5 by addition of alkali, the major species in solution is *cis*-Pt($^{15}NH_3$)$_2$(OH_2) (δ_{Pt} −1572, δ_N −76.9, J_{Pt-N} = 293 Hz), as reported previously.[5] However, in fresh solutions, a small proportion (5–10%) of a different species has been detected by ^{195}Pt and ^{15}N NMR. The ^{195}Pt spectrum shows a doublet of doublets at −1516.3 ppm and the ^{15}N spectrum two singlets with satellites. The Pt–N coupling constants, 298 and 334 Hz, correspond to ammine trans to terminal and bridging hydroxide, respectively. This species is therefore assigned as the deprotonated form of II, (Pt(NH_3)$_2$(OH))$_2$(μ-OH)$^+$.

The proportion of this compound, relative to Pt(NH_3)$_2$-(OH)$_2$, present initially probably depends on how quickly the pH was increased through the range 6–8, where rapid dimerization occurs. At pH 12.5, the concentration of the bridged species slowly decreased (over a period of several days).

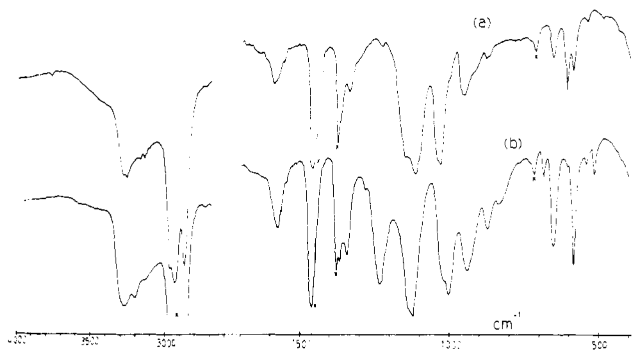

Figure 3. IR spectra of Nujol mulls of (a) *cis*-Pt(NH_3)$_2$(SO_4)(H_2O) and (b) *cis*-Pt(NH_3)$_2$(SO_4) (× = Nujol peaks).

Nitrato Complexes. When sodium nitrate is added to a solution of *cis*-[Pt($^{15}NH_3$)$_2$(H_2O)$_2$](ClO_4)$_2$, a new doublet of doublets is observed in the ^1H-decoupled ^{195}Pt NMR spectrum, to higher shielding than the triplet from I. In the ^1H-decoupled ^{15}N spectrum, apart from peaks due to I, a new singlet is observed, with two sets of satellites. There are, therefore, two nonequivalent ^{15}N nuclei in the nitrato complex, which "accidentally" have the same chemical shift. The simplest structure consistent with these spectra is III, with nitrate unidentate.

By analogy with other aqua complexes, the ^{15}N atom trans to water in III is assigned as that with the higher ^{195}Pt–^{15}N coupling constant (403.4 Hz). The lower value trans to nitrate (377.8 Hz) then indicates that nitrate has a slightly higher trans influence than water.

From integrated intensities of peaks in the ^{195}Pt NMR spectrum, the equilibrium constant for reaction 1 with A^{m-} = NO_3^- (ignoring [H_2O]) is 0.17 mol^{-1} L. Thus, a 0.5 M aqueous solution of *cis*-Pt(NH_3)$_2$(NO_3)$_2$ would be expected to contain 0.07 M of III, which is easily detected by NMR.

When excess sodium nitrate is added to a solution of I, or if a solution of the dinitrate is concentrated, solid *cis*-Pt(NH_3)$_2$(NO_3)$_2$ deposits. This compound has been shown to have structure IV by X-ray diffraction.[19] No peaks assignable to IV were observed in NMR spectra. Raman spectra of concentrated aqueous solutions of IV have shown weak peaks due to coordinated nitrate (as in III) as well as much stronger peaks from ionic nitrate.[19]

Sulfato Complexes. When sodium sulfate is added to a solution of *cis*-[Pt($^{15}NH_3$)$_2$(H_2O)$_2$](ClO_4)$_2$, a new doublet of doublets is observed in the ^1H-decoupled ^{195}Pt NMR spectrum, this time to lower shielding than I. The ^1H-decoupled ^{15}N spectrum shows two singlets with satellites (and peaks from I). The simplest structure giving nonequivalent ^{15}N nuclei is V, with sulfate unidentate.

Again, $^1J_{Pt-N}$ trans to sulfate (378.4 Hz) is slightly less than that trans to water (395.5 Hz).

From integrated intensities in ^{195}Pt and ^{15}N spectra, the equilibrium constant for reaction 1 with A^{m-} = SO_4^{2-} (ignoring [H_2O]) was calculated as 1.7 mol^{-1} L at 28 °C. A 0.5 M solution of Pt(NH_3)$_2$(SO_4) would therefore contain approximately 0.1 M V.

Evaporation to dryness of a solution of *cis*-[Pt(NH_3)$_2$-(H_2O)$_2$]SO_4 at room temperature under a stream of nitrogen yielded a solid that was analyzed as Pt(NH_3)$_2$(SO_4)(H_2O), apparently corresponding to the material obtained by King[20]

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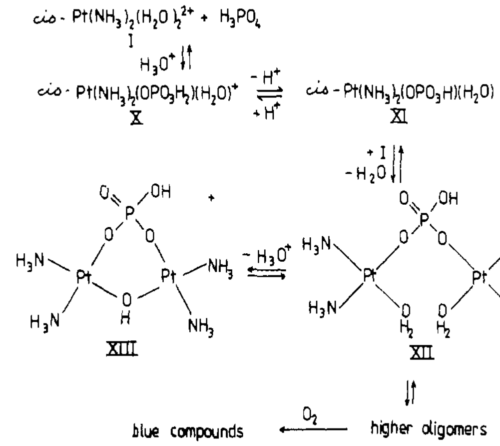
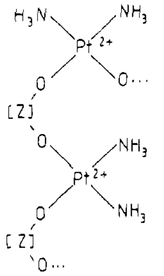
Scheme I



by evaporation in a vacuum desiccator. Its IR spectrum in the ν_{S-O} region (Figure 3a) shows bands at 958, 1033, 1118, and 1150 (shoulder) cm^{-1}, very similar to the spectrum reported by Eskenazi et al.[21] for $Pd(NH_3)_2(SO_4)(H_2O)$, and is consistent with the presence of unidentate sulfate, as in V.[20] Precipitation from hot solution gives anhydrous $Pt(NH_3)_2(SO_4)$, which gives a very different IR spectrum (Figure 3b), with bands at 940, 1000, 1015 (shoulder), 1120, 1130 (shoulder), and 1230 cm^{-1}. The spectrum is quite different from that reported for anhydrous $Pd(NH_3)_2(SO_4)$, where the highest frequency band occurs at 1195 cm^{-1}.

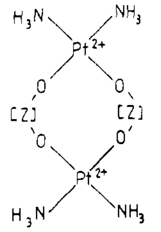
There are three structures possible for $Pt(NH_3)_2(SO_4)$ that retain the cis configuration of the ammine ligands: an infinite chain with bridging sulfate (VI), a dimer with bridging sulfate (VII), and a monomer with chelated sulfate (VIII). Since chelated and bridging sulfate each has C_{2v} symmetry, IR spectra do not allow an unequivocal structural assignment to be made. Nakamoto,[22] following Eskenazi et al.,[21] has suggested that only chelated sulfate gives a ν_{S-O} band above 1200 cm^{-1}. That this rule is not generally applicable is, however, evident from the IR spectra of the Pt(III) compounds $K_2[Pt_2(\mu-SO_4)_4L_2]$ (IX), which give bands at 1285–1300 cm^{-1}.[23]



VI $[Z]O_2 = SO_4^{2-}$

XV PO_4H^{2-}

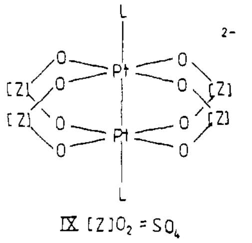
XX $O_2CCH_3^-$



VII $[Z]O_2 = SO_4^{2-}$

XVI PO_4H^{2-}

XXI O_2CCH_3



IX $[Z]O_2 = SO_4$

XIV PO_4H

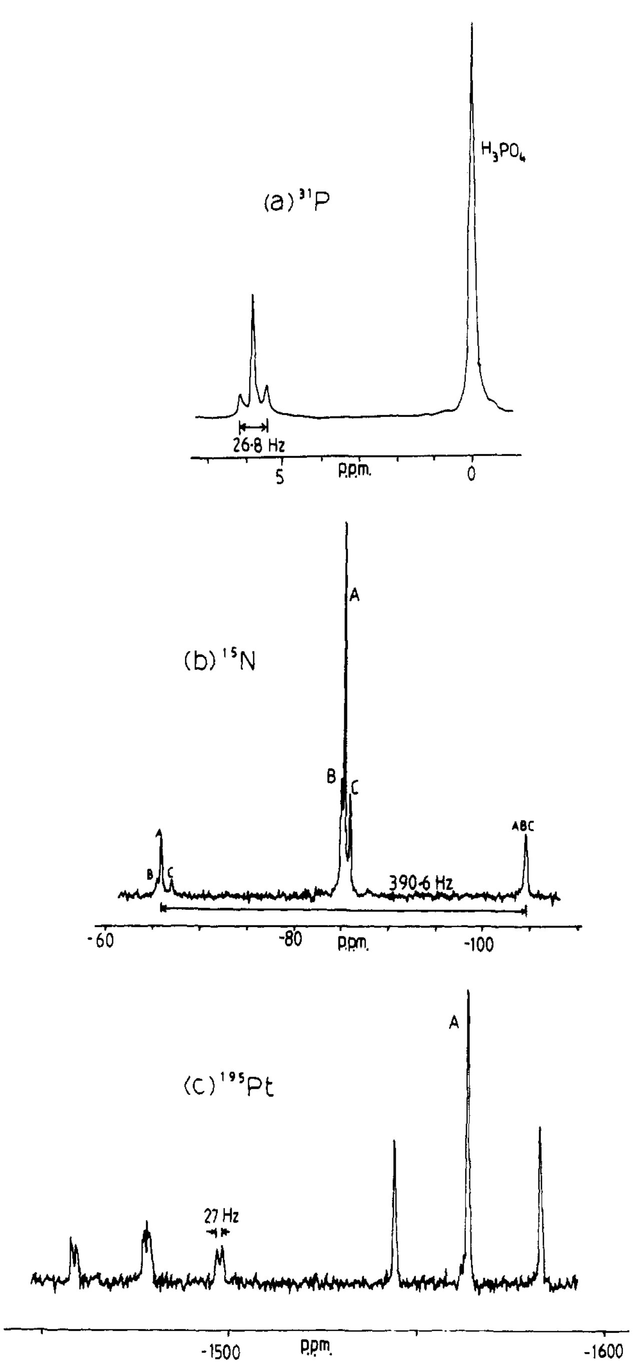


Figure 4. NMR spectra run on same solution, initially 0.20 M cis-$[Pt(^{15}NH_3)_2(H_2O)_2](ClO_4)_2$ and 0.21 M NaH_2PO_4, with the pH adjusted to 1.5: (a) ^{31}P; (b) ^{1}H-decoupled ^{15}N (peaks labeled A correspond to cis-$Pt(^{15}NH_3)_2(H_2O)_2{}^{2+}$ (I), B to ammine trans to H_2O, and C to ammine trans to $H_2PO_4^-$); (c) ^{1}H-decoupled ^{195}Pt (label A as for (b)). (a) and (b) are on the same frequency scale, and the scale of (c) is one-fifth of these.

Addition of excess sodium sulfate to an aqueous solution causes precipitation of $Pt(NH_3)_2(SO_4)(H_2O)$. No peaks due to a bis(sulfato)complex were observed.

Phosphato Complexes (Scheme I). Wood, Hunt, and Balch[9] have illustrated some ^{195}Pt and ^{31}P NMR spectra from solutions of cis-$Pt(^{15}NH_3)_2(H_2O)_2{}^{2+}$ and phosphate but concluded that "further identification of the structural characteristics of these complexes would involve premature speculation". By careful control of conditions, and the comparison of ^{195}Pt, ^{15}N, and ^{31}P spectra on the same solution (as

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in Figure 4), we have been able to identify the major species in these solutions. We were aided in this by the observation that much better quality ^{31}P spectra are obtained in acid solutions for this system. Many phosphate species give quite broad peaks in the presence of platinum(II) ammine complexes at pH 2–4. The effect is evident even in the spectrum of free phosphate in the presence of $[Pt(NH_3)_4]Cl_2$ and may be due to specific P–O···H–N hydrogen bonding once the phosphate species is deprotonated. Although most of the phosphate complexes are decomposed at pH 1.5, the reactions are quite slow (except, of course, protonation equilibria), so that it is often helpful to add acid to a solution to give a much improved spectrum. In acid solution (pH 1.5), Pt–O–P coupling has been clearly resolved for some species in our spectra, although Balch et al. did not resolve it.

If aqueous solutions of *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](ClO_4)_2$ and NaH_2PO_4 are mixed, to give a solution 0.2 M in each, and the pH is immediately adjusted to 1.5 with $HClO_4$, the ^{31}P NMR spectrum shows, in addition to a peak due to H_3PO_4, a sharp (width 5 Hz) singlet with satellites to lower shielding ($^2J_{Pt-O-P} = 26.8$ Hz) (Figure 4a). If phosphate were bridging between two Pt atoms, additional peaks would be expected from those complexes where phosphate was coordinated to two ^{195}Pt atoms. Spectra run at high amplitude did not show these additional peaks. Phosphate is therefore bound to only one Pt atom.

The ^1H-decoupled ^{15}N spectrum (Figure 4b) shows, in addition to peaks due to I, two singlets with satellites. The ^{15}N atoms are therefore nonequivalent, inconsistent with a structure in which phosphate forms a four-membered chelate ring. One Pt–N coupling constant (392.6 Hz) may be assigned to ammine trans to water, while the second coupling constant, 377.2 Hz, is comparable to that trans to sulfate in V.

The ^1H-decoupled ^{195}Pt spectrum shows, in addition to peaks from I, a doublet of doublets of doublets (Figure 4c), with splittings corresponding to the Pt–N and Pt–O–P coupling constants measured from ^{15}N and ^{31}P spectra, respectively. This confirms that only one phosphate ion is bound per Pt atom (since two equivalent phosphate ligands would give a triplet).

Addition of further acid causes a slow decrease in the intensities of peaks due to the compound, but no significant shifts. Increasing the pH does, however, cause shifts (see below).

These data are all consistent with the assignment of the species present as *cis*-$Pt(^{15}NH_3)_2(PO_4H_2)(H_2O)^+$ (X).

If this solution is allowed to stand at pH 1.5, it remains colorless, no additional peaks appear in the spectra, and no solid compounds deposit.

When the pH is increased to 4.5 by addition of NaOH solution, the ^{31}P peak broadens (to width 28 Hz) and shifts to lower shielding, as X deprotonates to XI. The ^{195}Pt resonance shifts to higher shielding (Table I), and the ^{15}N peaks become coincident with those from I. Because of this overlap, and the rapid growth of other peaks, Pt–N coupling constants could not be assigned with confidence.

If this solution is allowed to stand, the pH slowly decreases to an equilibrium value near 2.5, and new peaks appear in the ^{31}P spectrum. The most intense of these is a singlet without resolved satellites, whose chemical shift (7.91 ppm) is independent of pH over the range 0.5–5.0. The peak slowly decreases in intensity if pH is reduced below 2.5. The ^1H-decoupled ^{195}Pt spectrum also shows a new doublet of doublets. From comparisons of relative intensities of peaks due to this species and those from XI in ^{31}P and ^{195}Pt spectra, it can be deduced that the compound contains two Pt atoms per phosphate ligand.

Peaks due to this species also grow in the ^1H-decoupled ^{15}N spectrum—two singlets with satellites, from nonequivalent ^{15}N nuclei. However, both of the Pt–N coupling constants, 366 and 343 Hz, are too low to allow the complex to be assigned as $(Pt(NH_3)_2(H_2O))_2(\mu\text{-}PO_4H)^{2+}$ (XII), since, as shown above, J_{Pt-N} trans to water occurs in the range 390–404 Hz. Since, as in II, J_{Pt-N} trans to bridging hydroxide is near 340 Hz, and a value of 366 Hz is reasonable for ammine trans to bridging PO_4H^-, structure XIII is consistent with these spectra. That complexes with bridging hydroxide can exist near pH 3 is evident from the long lifetime of II under these conditions (see above).

^{31}P spectra of these solutions always show a peak at 5.42 ppm, independent of pH between 1.0 and 4.0, which appears to form before the peak due to XIII and to persist longer at pH 1–2. ^{15}N peaks at −84.86 and −85.34 ppm appear to correspond to this species also. No definite ^{195}Pt peaks were assigned, and no Pt–N coupling constants could be measured with confidence. It is possible that these peaks are due to $(Pt(NH_3)_2(H_2O))_2(\mu\text{-}PO_4H)^{2+}$ (XII). If so, this ion is never more than a minor component in the solution.

If a solution is allowed to stand with pH maintained near 3, a multitude of peaks, some quite broad, grow in the ^{31}P spectrum, with many peaks also evident in ^{15}N spectra. This can only be due to formation of oligomeric phosphate-bridged species (since the number of monomers and dimers possible is limited). If the solution is exposed to air, it slowly turns blue, and some blue solids precipitate. We have proposed[8] that the blue color is due to the oxidation of some platinum ions in oligomers, with some Pt atoms held in close proximity by Pt–O–P–O–Pt bridging, analogous to the "amide blues" (e.g., α-pyridone blues[24]), which have Pt–N–C–O–Pt bridges. The presence of phosphate bridges has been recently shown in the Pt(III) compound, $Na_2[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]$ (XIV).[25,26]

^{31}P spectra of methylamine analogues under comparable conditions are very similar to those of the ammine complexes (Table II). However, no solids, white or blue, precipitate from solution. This allows spectra to be obtained under conditions where it is difficult with the ammine system. If, for example, the pH of a solution from *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ and phosphate is maintained near 6, most of the material in solution eventually precipitates. This does not occur with methylamine, and the ^{31}P spectrum of a solution kept at pH 6 shows the analogue of XIII as the only significant species in solution.

Another difference with methylamine is that solutions kept in the dark do not turn blue. Prolonged exposure to visible light (3 days under normal laboratory lighting) is required. A short exposure to intense UV irradiation is ineffective.

Colorless and blue solutions at the same pH give similar ^{31}P spectra. Because blue compounds are paramagnetic, NMR peaks may well be too broad to be observed. Even so, it is likely that blue compounds are relatively minor components of the solutions.

There are also many parallels between ^{31}P spectra of 1,2-diaminoethane (en) analogues and the spectra discussed above, except that near pH 3 a number of ^{31}P peaks are present of comparable intensity (instead of the spectrum being dominated by peaks due to XI and XIII). In these circumstances, no assignment of peaks to the analogue of XIII was made.

Solutions of $Pt(en)(H_2O)_2^{2+}$ with phosphate readily turn blue in the dark and deposit small amounts of solid. This contrasts with $Pd(en)(H_2O)_2^{2+}$, which rapidly and quantitatively gives a precipitate of composition $Pd(en)(PO_4H)$. There are the same three types of structures possible as for anhydrous *cis*-$Pt(NH_3)_2(SO_4)$–analogues of XV, XVI, and a chelate. The

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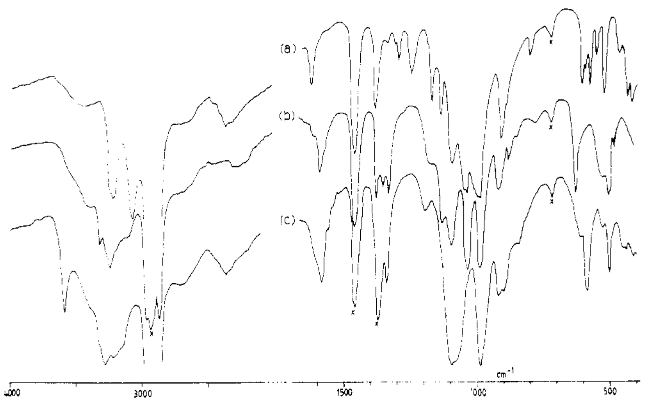


Figure 5. IR spectra of Nujol mulls of (a) Pd(en)(PO_4H), (b) white $Pt(NH_3)_2(PO_4H)\cdot 0.5H_2O$, (c) blue $Pt(NH_3)_2(PO_4H)\cdot 0.5H_2O$ (× = Nujol peaks).

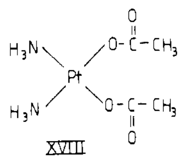
IR spectrum (Figure 5a) shows a broad weak band at 2380 cm^{-1} characteristic of hydrogen phosphates.[25] In the ν_{P-O} region, bands are present (with some additional minor splittings) at 910, 995, 1040, and 1092 cm^{-1}). Bands at 1139 and 1172 cm^{-1} could be due to phosphate or to the diamine ligand. (Pd(en)Cl_2 has sharp peaks of moderate intensity at 1060, 1110, and 1170 cm^{-1}.)

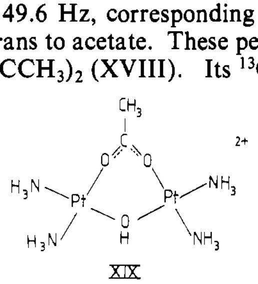
A grayish white solid may be obtained reproducibly from solutions of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ and phosphate at pH 2.5, which is too acid for much blue compound to form. The compound was analyzed as $Pt(NH_3)_2(PO_4H)\cdot 0.5H_2O$. Its IR spectrum (Figure 5b)[27] shows a broad band at 3400 cm^{-1}, which can be assigned to ν_{O-H}, ν_{N-H} peaks at 3315 and 3240 cm^{-1}, and a broad weak band at 2280 cm^{-1}. In the ν_{P-O} region, the spectrum is very similar to that of the palladium complex, with bands at 915, 985, 1030, 1095, 1130, and 1175 cm^{-1}. It is therefore likely that the structure is similar to that of the palladium complex and that water is only incorporated in the lattice.

It is surprising that the IR spectrum of the blue solid isolated, also analyzed as $Pt(NH_3)_2(PO_4H)\cdot 0.5H_2O$ (Figure 5c),[27] appears simpler in the ν_{P-O} region, with bands at 896, 916, 985, 1095, and 1195 (weak) cm^{-1}. That most of the phosphate present is still protonated is evident from the presence of a band at 2360 cm^{-1}. As well as broad ν_{N-H} peaks, the spectrum also shows a sharp ν_{O-H} band at 3575 cm^{-1}.

Acetato Complexes. ^{195}Pt and ^{15}N NMR spectra run on a solution prepared by mixing equimolar amounts of *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](NO_3)_2$ and sodium acetate show that most of the diaqua complex (I) quickly reacts to give a complex that shows a doublet of doublets in its platinum spectrum and two singlets with satellites in its nitrogen spectrum. One Pt–N coupling constant, 393.6 Hz, clearly corresponds to ammine trans to water. The other, 348.1 Hz, is significantly lower than for ammine trans to nitrate (378 Hz). Acetate has an NMR trans influence significantly higher than for nitrate,[28] so this peak is assigned to ammine trans to unidentate acetate. This species may therefore be assigned as *cis*-$Pt(^{15}NH_3)_2(O_2CCH_3)(H_2O)^+$ (XVII). Its ^1H-decoupled ^{13}C spectrum shows two singlets with satellites, due to methyl (δ_C 23.09, $^3J_{Pt-O-C-C}$ = 32.3 Hz) and carboxyl (δ_C 183.49, $^2J_{Pt-O-C}$ = 30 Hz) carbon atoms. The NMR parameters may be compared with those reported for $Pt(^{15}NH_3)_2$(ethylmalonate),[29] δ_{Pt} −1694, J_{Pt-N} = 366 Hz.

When larger quantities of acetate are added, a new set of peaks grows, which eventually becomes dominant. The ^{15}N spectrum is a singlet with satellites and the ^{195}Pt spectrum a 1:2:1 triplet, with J_{Pt-N} = 349.6 Hz, corresponding to two equivalent ammine ligands trans to acetate. These peaks are assigned to *cis*-$Pt(NH_3)_2(O_2CCH_3)_2$ (XVIII). Its ^{13}C spectrum shows peaks at 23.24 and 183.10 ppm, each with satellites ($^3J_{Pt-O-C-C}$ = 31 Hz, $^2J_{Pt-O-C}$ = 24.4 Hz). The ^1H spectrum in D_2O shows a singlet at 1.97 ppm. The ^{195}Pt and ^{15}N spectra of a solution with the Pt:acetate ratio 1:2 also showed peaks of significant intensity due to $[Pt(^{15}NH_3)_2(\mu\text{-}OH)]_3^{3+}$.


XVIII


XIX

For solutions with higher Pt:acetate ratios, numerous weaker peaks appeared with time. The most important set was a doublet of doublets to low shielding (−1548 ppm) in the platinum spectrum, with two singlets and satellites in the nitrogen spectrum. One Pt–N coupling constant, 377 Hz, could correspond to ammine trans to bridging acetate, which would be expected to have a lower trans influence than unidentate acetate. The other coupling constant, 351 Hz, could correspond to ammine trans to unidentate acetate, but this would require a complex $(Pt(NH_3)_2(O_2CCH_3))_2(\mu\text{-}O_2CCH_3)^+$ to be present in moderately high concentration in solutions containing the aqua complexes I and XVII. The shifts in ^{15}N and ^{195}Pt spectra compared with those for XVII are reminiscent of those for XIII compared with XI. The 351-Hz coupling is therefore assigned to ammine trans to bridging hydroxide in $(Pt(^{15}NH_3)_2)_2(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)_2^+$ (XIX). A singlet in the ^1H spectrum at 2.05 ppm may be assigned to this complex, but no definite ^{13}C assignments have been possible. The pH of these solutions is between 4 and 5.

Although it is a nonelectrolyte, *cis*-$Pt(NH_3)_2(O_2CCH_3)_2$ does not precipitate out from these solutions (~0.2 M). *cis*-$Pt(NH_3)_2(O_2CCH_3)_2\cdot 2H_2O$ may be obtained as a pale yellow solid by reaction of *cis*-$Pt(NH_3)_2Cl_2$ with silver acetate. It is quite soluble in water, slowly coming to equilibrium with *cis*-$Pt(NH_3)_2(O_2CCH_3)(OH_2)^+$ and free acetate. The solid shows strong, broad IR bands at 1621, 1578 (ν_{C-O} asym), 1366, and 1326 (ν_{CO} sym) cm^{-1}. The wide separation between asymmetric and symmetric stretching bands is consistent with the presence of unidentate acetate.[30]

When acetate is added to a solution of *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](ClO_4)_2$, rather than the nitrate salt, similar spectra are obtained, but after 10–20 min bright yellow filamentous crystals begin to deposit. This solid was analyzed as $Pt(NH_3)_2(O_2CCH_3)(ClO_4)\cdot H_2O$. Its IR spectrum shows a strong, broad perchlorate band at 1090 cm^{-1}, a broad ν_{O-H} band at 3540 cm^{-1}, and a broad ν_{N-H} band at 3310 cm^{-1}. ν_{C-O} bands occur at 1445 and 1540 cm^{-1} (with a shoulder at 1480 cm^{-1} probably due to δ_{NH_3}). These frequencies are in the range typical of bridging acetate,[30] so again it is probable that the water present is in the lattice. The structure could be an infinite chain (XX) or a dimeric unit (XXI).

The yellow solid readily redissolves in hot water, but continued heating in air causes solutions to turn dark blue-black. This is clearly related to the formation of "phosphate blues" described above, with oligomers containing Pt–O–C–O–Pt bridges being partially oxidized.

The complexity of the acetate system contrasts with the simple behavior of malonate, which gives a sparingly soluble chelate whose biological activity has been extensively investigated.[31]

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(27) The labels (a) and (b) should be interchanged in Figure 2 of ref 8.

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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.

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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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