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Aspects of the Solution Chemistry of *trans*-Diammineplatinum(II) Complexes[1]

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A convenient method for small-scale preparations of *trans*-$[PtCl_2(NH_3)_2]$ (e.g., for preparing ^{15}N-labeled compounds) is to heat $[Pt(NH_3)_4]Cl_2$ at 190–195 °C, under vacuum. ^{15}N and ^{195}Pt NMR spectra have been used to characterize in solution *trans*-diammineplatinum(II) complexes with aqua, chloro, nitrato, sulfato, acetato, and phosphato ligands. A solution of *trans*-$[Pt(OH)(H_2O)(NH_3)_2]^+$ allowed to stand gives a precipitate $[\{trans\text{-}Pt(\mu\text{-}OH)(NH_3)_2\}_n](NO_3)_n$. ^{15}N NMR spectra have been used to determine acid dissociation constants for *trans*-$[Pt(H_2O)_2(^{15}NH_3)_2]^{2+}$ (pK_{a1} 4.35, pK_{a2} 7.40) and for *trans*-$[PtCl(H_2O)(^{15}NH_3)_2]^+$ (pK_{a1} 5.63).

Introduction

Since the initial discovery that *cis*-$[PtCl_2(NH_3)_2]$ is active against some tumors while the trans isomer is inactive,[2] there has been considerable interest in the reactions of both isomers and their hydrolysis products with molecules of biological significance, including nucleobases,[3] oligo- and polynucleotides,[4,5] and amino acids and peptides.[6–8] Paralleling this progress in bioinorganic chemistry, the applications of X-ray crystallography,[9–12] UV spectroscopy combined with potentiometric measurements,[13–15] and multinuclear NMR spectroscopy[16–21] have thrown considerable light on the solution chemistry of *cis*-diammine- and *cis*-bis(amine)platinum(II) complexes. The fundamental solution chemistry of *trans*-diammineplatinum(II) complexes has been relatively unexplored. In this paper, we describe the results of a ^{15}N and ^{195}Pt NMR spectroscopic study of the chemistry of some *trans*-diammineplatinum(II) complexes, using ammine ligands highly enriched (>98%) in ^{15}N.

Experimental Section

The preparative procedures described below are for ^{15}N-enriched materials. The same procedures were also used to prepare complexes containing ^{14}N, except that it was not then necessary to employ measures to conserve ammonia (e.g., condensation of evolved ammonia gas).

Starting Materials. $(^{15}NH_4)_2SO_4$ (>98% ^{15}N) (Cambridge Isotopes) was supplied by Novachem (Melbourne, Australia). To obtain an aqueous solution of $^{15}NH_3$, a column of Amberlite IRA-400 (Cl) resin was converted to the hydroxide form by elution with 1 M NaOH solution and then washing with water. A concentrated solution of $(^{15}NH_4)_2SO_4$ was then added to the column and washed through with water until the eluted solution was no longer alkaline. The quantity of $^{15}NH_3$ eluted was calculated from the original weight of $(^{15}NH_4)_2SO_4$ added to the column. *cis*-$[PtCl_2(^{15}NH_3)_2]$ was prepared as previously described.[17,19]

Preparation of $[Pt(^{15}NH_3)_4]Cl_2$. To a suspension of *cis*-$[PtCl_2(^{15}NH_3)_2]$ (2.014 g, 6.67 mmol) in water was added an aqueous solution containing $^{15}NH_3$ (20 mmol). The mixture was heated under reflux until a clear solution was obtained, which was filtered. Water and ammonia were then distilled off (with the ammonia absorbed in dilute HCl solution, so that $^{15}NH_4Cl$ could be recovered) until the volume was small. Ethanol was added to precipitate a colorless solid, which was filtered off and then dried under vacuum over silica gel to give $[Pt(NH_3)_4]Cl_2$ (2.032 g, 90.1% yield). If the sample is not dried under vacuum, the compound is obtained as a hydrate, $[Pt(NH_3)_4]Cl_2\cdot H_2O$.[22]

Preparation of *trans*-$[PtCl_2(^{15}NH_3)_2]$. Anhydrous $[Pt(^{15}NH_3)_4]Cl_2$ (2.032 g) was placed in a Schlenk tube, which was then connected to a vacuum line through a liquid-nitrogen-cooled trap containing frozen 1 M HCl solution. The tube was placed in an oil bath maintained at 190–195 °C for 5 h. The resultant yellow solid was washed onto a sintered-glass funnel with water (to remove traces of water-soluble compounds), washed with acetone, and air-dried; yield 1.781 g (98.5%). We have successfully used this procedure to prepare quantities ranging from 0.1 to 5 g. With larger quantities, the tube should be shaken from time to time, to provide more uniform heating, and a slightly longer heating time may be required to ensure complete reaction.

If the tetraammineplatinum(II) salt was slightly moist, or if water of crystallization was not removed before the sample was heated at 190 °C, some decomposition occurred. This was easily avoided if the tube containing the solid was evacuated and the temperature of the surrounding oil bath was then slowly increased from room temperature. All water was lost before the bath reached 180 °C, and there was no decomposition.

Preparation of *trans*-$[Pt(ONO_2)_2(^{15}NH_3)_2]$. An aqueous suspension of *trans*-$[PtCl_2(^{15}NH_3)_2]$ (1.787 g, 5.92 mmol) in 10 mL of water was heated with a solution of silver nitrate (2.010 g, 10.84 mmol) in 20 mL of water, with stirring, protected from light, under nitrogen, at 90 °C for 48 h. The mixture was allowed to cool, and silver chloride was filtered off. The filtrate was taken to dryness in a rotary evaporator. The resulting pale yellow solid was washed with *cold* water to remove any remaining traces of silver nitrate, and then washed with acetone, and air-dried; yield 1.63 g (77.6%).

Preparation of *trans*-$[\{Pt(\mu\text{-}SO_4)(NH_3)_2\}_n]$. The preparation was similar to that of the nitrato complex described above, except that silver sulfate was used, rather than silver nitrate. If the removal of solvent water occurred at room temperature, a hygroscopic solid formed. If the solution was taken to dryness at 60–80 °C, an off-white solid was obtained, which did not absorb atmospheric moisture.

Preparation of *trans*-$[Pt(O_2CCH_3)_2(NH_3)_2]$. *trans*-$[PtCl_2(NH_3)_2]$ (0.50 g, 1.67 mmol) was suspended in 80 mL of water containing silver

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acetate (0.56 g, 3.30 mmol; supplied by BDH), and the mixture was heated at 90 °C under nitrogen for 48 h. The solution was cooled and silver chloride filtered off. The volume of the filtrate was decreased to 10 mL with the use of a rotary evaporator. The solution was then allowed to evaporate slowly in the dark in a vacuum desiccator over silica gel until colorless platelike crystals formed. These quickly crumbled once removed from the mother liquor, as water of crystallization was lost. After drying at ambient temperature in the vacuum desiccator, the composition of the solid corresponded to *trans*-$[Pt(O_2CCH_3)_2(NH_3)_2]\cdot 0.5H_2O$.

Preparation of *trans*-$[\{Pt(\mu\text{-}PO_4H)(NH_3)_2\}_n]$. *trans*-$[Pt(ONO_2)_2(NH_3)_2]$ (0.10 g, 2.8 mmol) was dissolved (by warming) in 2 mL of water. Solid $Na_2HPO_4\cdot 12H_2O$ (0.10 g, 2.8 mmol) was added to the solution, which was stirred for 4 h. During this time, an off-white solid precipitated. The solid was isolated by centrifugation, and then washed with water, ethanol, and ether, and dried under vacuum to give 0.05 g of product (55% yield).

NMR Spectra. The 10.1-MHz ^{15}N, 21.4-MHz ^{195}Pt, and 40.3-MHz ^{31}P NMR spectra were obtained as previously described.[19,20] Unless otherwise state, ^{15}N and ^{195}Pt spectra were ^1H-decoupled. References used: ^{15}N, a coaxial capillary containing 5 M $^{15}NH_4{}^{15}NO_3$ in 2 M HNO_3, with the ammonium ion signal taken as zero; ^{195}Pt, a separate sample containing 0.5 g of $Na_2[PtCl_6]$ in 2 mL of H_2O; ^{31}P, a coaxial capillary containing 85% H_3PO_4. Shifts are positive to lower shielding. The ^{15}N spectra were run at the lower field (i.e., 10.1 MHz) except for some of the measurements of δ_N as a function of pH, for which 40.4-MHz spectra allowed more precise measurement of small shifts. The effects of concentration and of other dissolved compounds affected δ_N up to ±0.05 ppm and ^{195}Pt shifts up to ±5 ppm. ^{195}Pt–^{15}N coupling constants were usually measured from ^{15}N spectra (reproducible to ±1 Hz).

Determination of Acid Dissociation Constants. To measure pH, a TPS digital pH meter fitted with a combination glass/reference electrode was used, calibrated at 298 K against phthalate (pH 4.01) and phosphate (pH 6.87) buffer solutions. For the measurements of variation of NMR parameters with pH, a 5-mL sample was used. The pH was adjusted to the desired value with NaOH or HNO_3 solution, and a 2-mL aliquot was removed and placed in the NMR tube (10-mm diameter). The electrode remained immersed in the residual liquid. After the NMR measurement, the samples were again combined, and the pH recorded. Changes in pH during the measurement were usually very small; values before and after the measurement were averaged. More HNO_3, or NaOH, was then added, to adjust the pH to a new value. Concentration of platinum complexes was near 0.1 M. During the titration of *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$, the ionic strength varied between 0.3 and 0.2 M, and for the titration of *trans*-$[PtCl(H_2O)(^{15}NH_3)_2]^+$, it was approximately constant at 0.2 M. No attempt was made to correct pH readings for the effect of high ionic strength.

Results

Satisfactory analytical results were obtained for solids isolated. NMR data are presented in Table I.

NMR Spectra of *trans*-Diammineplatinum(II) Complexes. For all of the compounds discussed here, the two mutually trans ammine ligands bound to one platinum atom are equivalent and will therefore give a single peak in the ^{15}N NMR spectrum, with "satellites", from coupling with ^{195}Pt ($I = {}^1/_2$, 34% abundance). Because cis influences on δ_N and J(Pt–N) are both much smaller and less well understood than trans influences,[20] these parameters are less useful for characterization purposes than for *cis*-diammine complexes in which it is the ligands trans to ammine which are varied. Nevertheless, the sharpness of the peaks and the observation in a small frequency "window" of a peak from each distinct compound present make ^{15}N NMR spectroscopy very useful in monitoring reactions. The ^{195}Pt NMR spectrum from each distinct platinum nucleus will be a 1:2:1 triplet from coupling with two equivalent ^{15}N nuclei, unless other nuclei are present which also couple with ^{195}Pt, or which broaden the signal (e.g., ^{14}N, through partial decoupling of ^{195}Pt from the quadrupolar ^{14}N nucleus[23]). The ^{195}Pt chemical shift usually allows the identification of at least the set of donor atoms bound to the metal.[20,24]

Table I. ^{15}N and ^{195}Pt NMR Data[a]

	δ_{Pt}[b]	δ_N	J(Pt–N),[c] Hz
trans-$[PtCl_2(NH_3)_2]$[d]	–2101	–66.3	278
cis-$[PtCl_2(NH_3)_2]$[d,e]	–2104	–65.9	303
trans-$[Pt(H_2O)_2(NH_3)_2]^{2+}$	–1374	–62.3	312
cis-$[Pt(H_2O)_2(NH_3)_2]^{2+}$[f]	–1584	–85.8	391
trans-$[Pt(ONO_2)(H_2O)(NH_3)_2]^+$	*g*	–62.0	323
trans-$[Pt(ONO_2)_2(NH_3)_2]$[d]	–1413	–62.7	331
trans-$[Pt(ONO_2)(dmf\text{-}O)(NH_3)_2]^+$[d]	–1355	–60.7	327
trans-$[Pt(dmf\text{-}O)_2(NH_3)_2]^{2+}$[d]	–1284	–64.6	301
cis-$[Pt(ONO_2)_2(NH_3)_2]$[d]	–1592	–85.7	370
cis-$[Pt(ONO_2)(dmf\text{-}O)(NH_3)_2]^+$[d]	–1588	–83.4	368
		–87.6	391
cis-$[Pt(dmf\text{-}O)_2(NH_3)_2]^{2+}$[d]	*g*	–85.2	*g*
trans-$[Pt(OSO_3)(H_2O)(NH_3)_2]$	–1334	–60.8	318
trans-$[Pt(OSO_3)_2(NH_3)_2]^{2-}$	–1292	–59.5	325
trans-$[Pt(OH)_2(NH_3)_2]$	–1385	–63.2	302
$[\{$*trans*-$Pt(H_2O)(NH_3)_2\}_2(\mu\text{-}OH)]^{3+}$	–1394	–58.4	301
$[\{$*trans*-$Pt(OH)(NH_3)_2\}_2(\mu\text{-}OH)]^+$	–1340	–58.4	301
trans-$[PtCl(H_2O)(NH_3)_2]^+$	–1783	–64.1	294
cis-$[PtCl(H_2O)(NH_3)_2]^+$[h]	–1841	–65.8	343
		88.9	369
trans-$[PtCl(OH)(NH_3)_2]$	–1776	–63.8	293
$[\{$*trans*-$PtCl(NH_3)_2\}_2(\mu\text{-}OH)]^+$	–1746	–59.2	297
trans-$[Pt(O_2CCH_3)(H_2O)(NH_3)_2]^+$	–1415	–63.53	308
trans-$[Pt(O_2CCH_3)_2(NH_3)_2]$	–1441	–64.57	319
$[\{$*trans*-$Pt(H_2O)(NH_3)_2\}_2(\mu\text{-}O_2CCH_3)]^{3+}$	*g*	–57.2	*g*
trans-$[Pt(OPO_3H_2)(H_2O)(NH_3)_2]^+$[i]	–1275	–61.3	315
trans-$[Pt(OPO_3H)(H_2O)(NH_3)_2]$	*g*	–61.0	314
trans-$[Pt(OPO_3H_2)_2(NH_3)_2]$	–1184	–60.4	312

[a] Spectra in H_2O unless otherwise indicated. [b] All patterns for trans isomers are 1:2:1 triplets. [c] From the ^{15}N spectrum. [d] In dmf. [e] From ref 17. [f] From ref 19. [g] Not measured. [h] From ref 21. [i] δ_P 6.48; J(Pt–P) = 24.4 Hz.

The Preparation of *trans*-$[PtCl_2(NH_3)_2]$. The preparative method which is used almost exclusively today is that of Kauffman and Cowan,[25] a refinement of one of the preparative methods known since the compound was first discovered,[26] viz., heating $[Pt(NH_3)_4]Cl_2$ with hydrochloric acid. While the yield claimed, 90%, can be achieved with careful control of the reaction conditions, this method, in our experience, does not work very well on the smaller scale, which is usually required when isotopically labeled ligands are used. The alternative procedure described by Reiset[26] is to heat solid $[Pt(NH_3)_4]Cl_2$. For over a century, this appears to have been the preferred method.[27-29] The usual procedure was to heat solid $[Pt(NH_3)_4]Cl_2$ in air at 250 °C for 30 min. However, this conversion was usually accompanied by significant decomposition to platinum metal, which gave the product a dark gray coloration. Although a pure product could be obtained by recrystallization from boiling dilute HCl, this decomposition reduced yields and led to the eventual fall of this method from favor.

Block et al.[22] showed that conversion from $[Pt(NH_3)_4]Cl_2$ to *trans*-$[PtCl_2(NH_3)_2]$ will occur without decomposition at lower temperatures (up to 200 °C), but long times were required for complete conversion.

We have found that heating $[Pt(NH_3)_4]Cl_2$ under vacuum, rather than in air, at 190–195 °C, gives *trans*-$[PtCl_2(NH_3)_2]$ quantitatively in a reasonable time (within 5 h) and without any detectable decomposition. When labeled ammonia is used, this method has the additional advantage that the ammonia evolved can be condensed under vacuum and recovered. If heating is prolonged (>12 h) some slow decomposition occurs. Decomposition is faster above 200 °C.

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The product prepared as described above is sufficiently pure for most purposes, without recrystallization. Although this method is especially useful for preparations on a small scale, it is also, in our experience, convenient for the routine preparation of *trans*-$[PtCl_2(NH_3)_2]$ on a larger scale. After we had established the conditions needed to prepare the *trans*-diammine complex, we learned[30] that heating $[PtL_4]X_2$ under vacuum is a useful procedure for preparing *trans*-$[PtX_2L_2]$ complexes with some other ligands, L (e.g., pyridine).

trans-$[PtCl_2(NH_3)_2]$ is very sparingly soluble in water at room temperature but dissolves readily in *N,N*-dimethylformamide (dmf). ^{15}N and ^{195}Pt NMR parameters for *trans*-$[PtCl_2(^{15}NH_3)_2]$ in dmf are given in Table I, with those for the cis isomer in dmf,[17] for comparison.

Diaqua and Nitrato Complexes. The removal of both chloride ions from *trans*-$[PtCl_2(NH_3)_2]$ requires more forcing conditions than for the cis isomer. In our experience, prolonged heating with silver ion at 90 °C or above is necessary. Similar observations were made long ago. Cleve in 1872[31] erroneously reported that silver nitrate does not precipitate all chloride. King (1938)[28] corrected him, reporting that removal of the chloride ions from *trans*-$[PtCl_2(NH_3)_2]$ requires refluxing with a silver salt solution, while the cis isomer requires only a few hours' stirring at room temperature. Nevertheless, some more recent authors[32,33] have attempted to abstract chloride from *trans*-$[PtCl_2(NH_3)_2]$ using the mild conditions appropriate to the cis isomer. Under these conditions, complete reaction was unlikely.

Our reactions involving prolonged heating of *trans*-$[PtCl_2(NH_3)_2]$ with silver salts were always carried out under nitrogen, after some early experiments in air gave products with NMR peaks corresponding to platinum(IV) products.

Concentration of an aqueous solution of *trans*-$[Pt(H_2O)_2(^{15}NH_3)_2](NO_3)_2$ prepared in this way gave a solution whose ^{195}Pt NMR spectrum showed the expected 1:2:1 triplet and whose ^{15}N spectrum showed a singlet with satellites (Table I). The ^{1}H-coupled ^{195}Pt NMR spectrum showed, as expected, a triplet of septets. The $^{195}Pt-N-^{1}H$ coupling constant, 53.8 Hz, is significantly less than for *cis*-$[Pt(H_2O)_2(^{15}NH_3)_2]^{2+}$, 73.3 Hz.[19]

When a solution was taken to dryness on a rotary evaporator, *trans*-$[Pt(ONO_2)_2(^{15}NH_3)_2]$ was obtained as a cream-colored solid. It was almost insoluble in cold water but dissolved readily with heating and stirring, as reported by King.[28] The NMR spectra of the resultant aqueous solution corresponded to the diaqua complex. We have used the dinitrato complex as a convenient source of the diaqua complex. The crystal structure of *cis*-$[Pt(ONO_2)_2(NH_3)_2]$[9] showed that the nitrate ions are each coordinated to platinum through a single oxygen atom. The IR spectrum of the nitrato ligands in the trans isomer (strong bands at 1497, 1309, 1273, and 972 cm^{-1}) was very similar to that of the cis isomer,[9] but with less band splitting. The nitrate ions are undoubtedly bound in a similar way.

In an attempt to observe spectra of nitrato complexes in aqueous solution, excess potassium nitrate was added to a solution of *trans*-$[Pt(H_2O)_2(^{15}NH_3)_2](NO_3)_2$. Under these conditions, with the cis isomer, peaks from *cis*-$[Pt(ONO_2)(H_2O)(^{15}NH_3)_2]^+$ were readily observed.[19] However, with the trans isomer, peaks assigned to *trans*-$[Pt(ONO_2)(H_2O)(^{15}NH_3)_2]^+$ (Table I) were observed only after a solution saturated in KNO_3 was heated for 2 h. *trans*-$[Pt(ONO_2)_2(^{15}NH_3)_2]$ dissolved slowly in dmf at room temperature. The ^{15}N NMR spectrum of the solution showed a singlet with satellites and the ^{195}Pt NMR spectrum a 1:2:1 triplet, which were assigned to the dinitrato complex. When the solution was heated, additional peaks were observed which were assigned to the complexes *trans*-$[Pt(ONO_2)(dmf\text{-}O)(^{15}NH_3)_2]^+$ and *trans*-$[Pt(dmf\text{-}O)_2(^{15}NH_3)_2]^{2+}$, in which dmf is bound through the amide oxygen (Table I). Addition of $NaNO_3$ to the solutions without heating had little effect on the spectra.

For comparison, the behavior of *cis*-$[Pt(ONO_2)_2(^{15}NH_3)_2]$ in dmf was studied. Immediately on dissolution, ^{15}N and ^{195}Pt NMR spectra showed peaks due to each of the species *cis*-$[Pt(ONO_2)_2(^{15}NH_3)_2]$, *cis*-$[Pt(ONO_2)(dmf\text{-}O)(^{15}NH_3)_2]^+$, and *cis*-$[Pt(dmf\text{-}O)_2(^{15}NH_3)_2]^{2+}$ (Table I). Assignment of the peaks was aided by the changes observed on addition of $NaNO_3$ to the solution, which caused immediate growth in the peaks assigned to nitrato complexes. Hollis et al.[34] observed ^{195}Pt NMR peaks due to some of these species as minor components of solutions obtained by reaction of equimolar quantities of *cis*-$[PtCl_2(^{15}NH_3)_2]$ and $AgNO_3$ in dmf. The results of the experiments mentioned above have caused us to reverse their assignments for *cis*-$[Pt(ONO_2)_2(NH_3)_2]$ and *cis*-$[Pt(dmf\text{-}O)_2(NH_3)_2]^{2+}$. Otherwise, our results agree with theirs, within experimental error. None of the observed peaks was due to an aqua complex, as, when water was deliberately added to the solution, additional peaks appeared, and those described above decreased in intensity.

Sulfato Complexes. When sodium sulfate was added to an aqueous solution of *trans*-$[Pt(H_2O)_2(^{15}NH_3)_2](NO_3)_2$, and the solution was allowed to stand for 1 h, ^{15}N and ^{195}Pt NMR spectra showed, in addition to peaks from the diaqua complex, peaks assigned to *trans*-$[Pt(OSO_3)(H_2O)(^{15}NH_3)_2]$ (Table I). With further standing, much weaker ^{15}N NMR peaks were observed, (−56.5, −57.4 ppm), which were probably due to complexes containing bridging sulfate. With addition of more sulfate, the peaks due to $[Pt(OSO_3)(H_2O)(^{15}NH_3)_2]$ continued to grow, at the expense of those due to the diaqua complex. With a large excess of added sulfate (>2 mol equiv), and 24 h of standing, an additional set of peaks was observed, assigned to *trans*-$[Pt(OSO_3)_2(^{15}NH_3)_2]^{2-}$ (Table I). In a saturated sodium sulfate solution, these peaks were the only ones observed. With the cis isomer, peaks due to *cis*-$[Pt(OSO_3)(H_2O)(^{15}NH_3)_2]$ were readily observed when sulfate was added to a solution of the diaqua complex, but there were no peaks due to a bis(sulfato) complex.[19]

When a solution of *trans*-$[Pt(H_2O)_2(NH_3)_2]SO_4$ (from *trans*-$[PtCl_2(NH_3)_2]$ and Ag_2SO_4) was taken to dryness under reduced pressure at room temperature, a hygroscopic white solid was obtained, readily soluble in water. This appears to correspond to the product isolated by King,[28] which was formulated by him as *trans*-$[Pt(OSO_3)(H_2O)(NH_3)_2]$, with monodentate sulfate. A solution of *cis*-$[Pt(H_2O)_2(NH_3)_2]SO_4$ taken to dryness at room temperature similarly gave *cis*-$[Pt(OSO_3)(H_2O)(NH_3)_2]$, which also easily dissolves in water.[19] Rochon and Melanson[12] have described the crystal structure of an analogous complex, $[Pt(OSO_3)(H_2O)\{NH(CH_3)(CH_2)_2NH(CH_3)\}]$. If removal of solvent water from a solution of *trans*-$[Pt(H_2O)_2(NH_3)_2]SO_4$ was carried out at 60–80 °C, however, an off-white anhydrous solid was obtained. Its IR spectrum showed strong bands at 905 (with a shoulder at 917), 1012, 1036, 1119, and 1173 (with a shoulder at 1171) cm^{-1}. Its probable structure is an infinite linear polymer. Unlike anhydrous *cis*-$[Pt(SO_4)(NH_3)_2]$, which dissolves in water only with great difficulty,[19] *trans*-$[\{Pt(NH_3)_2(\mu\text{-}SO_4)\}_n]$ dissolved easily with gentle heating. It was insoluble in dmf.

Acid Dissociation of *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$. When NaOH solution was added rapidly to a solution (approximately 0.1 M) of *trans*-$[Pt(H_2O)_2(^{15}NH_3)_2](NO_3)_2$, to increase the pH from approximately 3 to 9, changes occurred in the ^{15}N and ^{195}Pt NMR spectra, corresponding to deprotonation of the coordinated aqua ligands, to give *trans*-$[Pt(OH)_2(^{15}NH_3)_2]$ (Table I). These changes were, as expected, much smaller in magnitude than the corresponding changes when water coordinated trans to ammine in *cis*-$[Pt(H_2O)_2(^{15}NH_3)_2]^{2+}$ is deprotonated.[17-21] At interme-

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diate values of pH, the spectra show concentration-weighted averages of the shifts and coupling constants of the three species, *trans*-$[Pt(H_2O)_2(^{15}NH_3)_2]^{2+}$ (AA), *trans*-$[Pt(OH)(H_2O)(^{15}NH_3)_2]^{+}$ (AB), and *trans*-$[Pt(OH)_2(^{15}NH_3)_2]$ (BB). The variation in these parameters may be used to determine the acid dissociation constants K_{a1} and K_{a2}.

$$trans\text{-}[Pt(H_2O)_2(NH_3)_2]^{2+} \overset{K_{a1}}{\rightleftharpoons} trans\text{-}[Pt(OH)(H_2O)(NH_3)_2]^{+} + H^{+} \quad (1)$$

$$trans\text{-}[Pt(OH)(H_2O)(NH_3)_2]^{+} \overset{K_{a2}}{\rightleftharpoons} trans\text{-}[Pt(OH)_2(NH_3)_2] + H^{+} \quad (2)$$

This determination is, however, complicated by the formation of hydroxo-bridged complexes. If a solution at pH 4 was allowed to stand, a new set of peaks appeared in the NMR spectra (more rapidly in concentrated solutions), assigned to $[\{trans\text{-}Pt(H_2O)(^{15}NH_3)_2\}_2(\mu\text{-}OH)]^{3+}$, analogous to previously-described complexes containing a single hydroxo bridge between Pt(II) atoms, $[\{cis\text{-}Pt(H_2O)(NH_3)_2\}_2(\mu\text{-}OH)]^{3+}$,[19] $[\{Pt(NH_3)_3\}_2(\mu\text{-}OH)]^{3+}$,[21] and $[\{Pt(dien)\}_2(\mu\text{-}OH)]^{3+}$.[35] If, once this dinuclear species had formed and was in equilibrium with *trans*-$[Pt(OH)(H_2O)_2(^{15}NH_3)_2]^{+}$, the pH was increased to 9, a significant shift occurred in δ_{Pt}, corresponding to deprotonation of the terminal aqua ligands, to form $[\{trans\text{-}Pt(OH)(^{15}NH_3)_2\}_2(\mu\text{-}OH)]^{+}$ (Table I). δ_N was unaffected by this deprotonation. The hydroxo-bridged species **2** persisted in solution if acid was added to decrease the pH to 2, but *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$ formed rapidly in more acidic solutions.

When the pH of a solution of *trans*-$[Pt(H_2O)_2(NH_3)_2](NO_3)_2$ was increased to 5–6 and the solution was allowed to stand, a white solid analyzing for $[Pt(OH)(NH_3)_2]NO_3$ was obtained, which was insoluble in water, alkali, and dmf but dissolved slowly in hot acidic solution. The IR spectrum of the solid showed peaks at 1390 and 1340 cm^{-1} corresponding to ionic nitrate. An analogous solid, analyzing for $[Pt(OH)(NH_3)_2]_2SO_4$, was obtained from the reaction of *trans*-$[Pt(H_2O)_2(NH_3)_2]SO_4$ with alkali. Its IR spectrum showed a broad band at 1100 cm^{-1} corresponding to ionic sulfate. We formulate these solids as containing hydroxo-bridged polymeric cations, $[\{Pt(\mu\text{-}OH)(NH_3)_2\}_n]^{n+}$, which could be linear or cyclic. Eventually, no peaks remained in the ^{15}N and ^{195}Pt NMR spectra of the supernatant solution.

The variation of NMR parameters with pH may be used to determine acid dissociation constants for *trans*-$[Pt(H_2O)_2(^{15}NH_3)_2]^{2+}$, provided that peaks from the mononuclear species remain visible. Measurements were carried out as quickly as possible in the mid-pH range. The variation of δ_{Pt} with pH is shown in Figure 1a. The plot clearly shows two regions where δ_{Pt} changes rapidly with pH. The experimental points were fitted to the best (least squares) values of pK_{a1}, pK_{a2}, and δ_{AB}, using the equation

$$\delta = (\delta_{AB} + \delta_{AA}[H^+]/K_{a1} + \delta_{BB}K_{a2}/[H^+])/(1 + [H^+]/K_{a1} + K_{a2}/[H^+]) \quad (3)$$

as previously described,[21] to give the acid dissociation constants listed in Table II.

The variation of δ_N with pH is shown in Figure 1b. It should be emphasized that the total change in δ_N, approximately 0.6 ppm, is quite small, much smaller than the corresponding change in δ_N (trans to H_2O/OH^-) when *cis*-$[Pt(H_2O)_2(^{15}NH_3)_2]^{2+}$ is deprotonated (approximately 9 ppm[21]). It is obvious from the plot that δ_N changes much more with the second deprotonation (eq 2) than with the first and that the changes are of opposite sign. The measurements on which Figure 1b was based were made with care on a high-field instrument (40.4 MHz) after earlier measurements at 10.1 MHz showed that the change in δ_N for the first deprotonation was, at best, very small. These observations provide a warning against arguments (e.g., that no deprotonation occurs over a certain pH range) based on negative evidence (e.g., the lack of a sharp change in chemical shift as the pH changes), especially if only one nucleus is being observed.

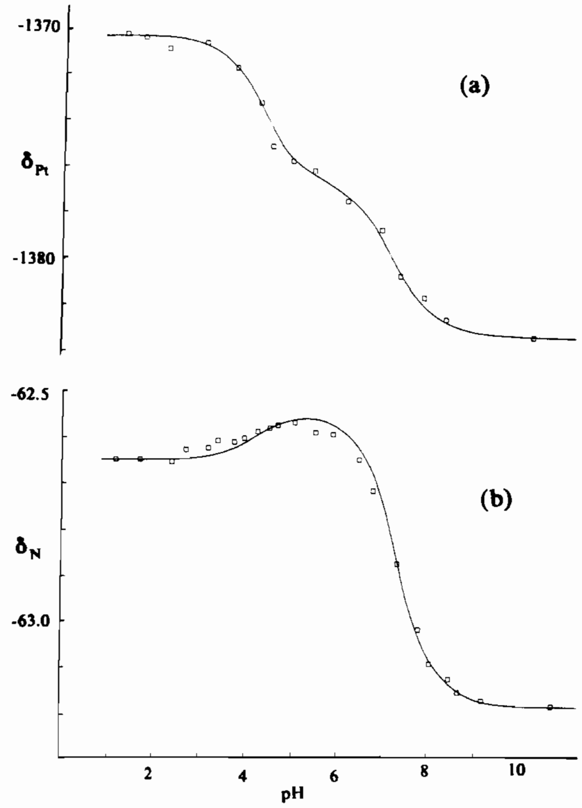

Figure 1. Variation of NMR chemical shifts in *trans*-$[Pt(H_2O)_2(^{15}NH_3)_2]^{2+}$ with pH: (a) δ_{Pt} (the curve is that calculated using δ_{AA} −1370.2, δ_{BB} −1383.1, δ_{AB} −1376.6, pK_{a1} 4.35, and pK_{a2} 7.40); (b) δ_N (the curve is that calculated with pK_a values as above and δ_{AA} −62.646, δ_{BB} −63.181, and δ_{AB} −62.450).

Table II. Acid Dissociation Constants for Platinum(II) Aqua Complexes

	temp, K	method	pK_{a1}	pK_{a2}	ref
cis-$[Pt(H_2O)_2(NH_3)_2]^{2+}$	278	NMR	5.93	7.87	21
trans-$[Pt(H_2O)_2(NH_3)_2]^{2+}$	298	NMR	4.35	7.40	*a*
	293	pot. titn	4.32	7.38	45
		pot. titn	7.20	10.00	44
	298?	pot. titn	4.23	7.30	46
$[Pt(H_2O)(NH_3)_3]^{2+}$	298	NMR	6.37		21
cis-$[PtCl(H_2O)(NH_3)_2]^{+}$	298	NMR	6.85		21
trans-$[PtCl(H_2O)(NH_3)_2]^{+}$	298	NMR	5.63		*a*
$[Pt(NO_2)_3(H_2O)]^{-}$	298	NMR	5.32		38

[a] This work.

The variation in J(Pt–N) with pH (not illustrated) did show sharp decreases in the magnitude of the coupling constant at the pH values corresponding to pK_{a1} and pK_{a2}, although the change was greater for the second deprotonation than for the first.

Chloro–Aqua Complexes. Solutions containing predominantly *cis*-$[PtCl(H_2O)(NH_3)_2]^{+}$ may be obtained by careful addition of sodium chloride to a solution of *cis*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$.[21] However, when an equimolar quantity of NaCl was added to a solution of *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$, only a trace of *trans*-$[PtCl(H_2O)(NH_3)_2]^{+}$ was obtained. Instead, approximately half of the complex reacted with 2 equiv of chloride, to form *trans*-$[PtCl_2(NH_3)_2]$ (most of which precipitated), leaving unreacted

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trans-$[Pt(H_2O)_2(NH_3)_2]^{2+}$ in solution. A solution containing predominantly (approximately 80%) *trans*-$[PtCl(H_2O)(^{15}NH_3)_2]^+$ (NMR parameters in Table I) was obtained by reaction of a stirred aqueous suspension of *trans*-$[PtCl_2(^{15}NH_3)_2]$ with an equimolar quantity of silver nitrate overnight. The solution obtained after removal of silver chloride was relatively stable if kept dilute (<0.1 M). More concentrated solutions underwent a chloride disproportionation reaction

$$2\ trans\text{-}[PtCl(H_2O)(NH_3)_2]^+ \rightarrow trans\text{-}[PtCl_2(NH_3)_2] + trans\text{-}[Pt(H_2O)_2(NH_3)_2]^{2+} \quad (4)$$

Addition of NaOH solution, to increase the pH of a solution of *trans*-$[PtCl(H_2O)(^{15}NH_3)_2]^+$ rapidly to 9, caused the expected deprotonation shifts (Table I). The ^{15}N and ^{195}Pt NMR spectra of a solution allowed to stand at pH 4.5–6 showed an additional set of peaks assigned to the dinuclear complex [{*trans*-PtCl-$(^{15}NH_3)_2\}_2(\mu\text{-}OH)]^+$ (Table I). These peaks rapidly disappeared on addition of acid, with peaks from *trans*-$[PtCl(H_2O)(^{15}NH_3)_2]^+$ again appearing. The acid dissociation constant for *trans*-$[PtCl(H_2O)(^{15}NH_3)_2]^+$ was determined from the variation of δ_N with pH, using the form of the Henderson–Hasselbach equation[36]

$$pK_a = pH + \log [(\delta - \delta_B)/(\delta_A - \delta)] \quad (5)$$

(where δ_A is the shift of the acid form and δ_B is the shift of the base form), as previously described[21,37,38] (Table II).

Phosphato Complexes. After phosphoric acid was added to a solution of *trans*-$[Pt(H_2O)_2(^{15}NH_3)_2]^{2+}$ (approximately equimolar quantities), there was slow growth of a new singlet with satellites in the ^{15}N and ^{195}Pt NMR spectra assigned to *trans*-$[Pt(OPO_3H_2)(H_2O)(^{15}NH_3)_2]^+$ (Table I). A singlet also appeared in the ^{31}P NMR spectrum at 6.48 ppm, with satellites from coupling to ^{195}Pt (24.4 Hz). When the solution was heated, a second set of weak peaks was observed, probably due to *trans*-$[Pt(OPO_3H_2)_2(^{15}NH_3)_2]$. The pH of this solution was <1. Addition of NaOH solution, to increase the pH of a solution of *trans*-$[Pt(OPO_3H)(H_2O)(^{15}NH_3)_2]^+$ to 3.5, caused a small shift in the ^{15}N NMR peak corresponding to deprotonation of the coordinated phosphate (Table I). Other weak peaks were present in the ^{15}N spectrum, probably due to species containing bridging phosphate. A precipitate then formed, which was insoluble in all solvents tested, except hot acid. It is likely that the compound is [{*trans*-$Pt(\mu\text{-}PO_4H)(NH_3)_2\}_n]$, with bridging phosphate groups. There was no formation of blue colors, as occurs with phosphate complexes of *cis*-diammineplatinum(II).[19,39]

Acetato Complexes. Addition of sodium acetate to an aqueous solution of *trans*-$[Pt(H_2O)_2(^{15}NH_3)_2](NO_3)_2$ (approximately equimolar quantities) caused the appearance, after long standing or warming, of ^{15}N and ^{195}Pt NMR peaks corresponding to *trans*-$[Pt(O_2CCH_3)(H_2O)(^{15}NH_3)_2]^+$ (Table I). These peaks increased in intensity when more acetate was added, and a new set of peaks also appeared, corresponding to *trans*-$[Pt(O_2CCH_3)_2(^{15}NH_3)_2]$. In solutions which contained excess diaqua complex, another ^{15}N peak was observed in addition to that from *trans*-$[Pt(O_2CCH_3)(H_2O)(^{15}NH_3)_2]^+$. Since the possible mononuclear complexes have been considered above, it is likely that this peak arises from a dinuclear complex with a bridging acetate, [{*trans*-$Pt(H_2O)(^{15}NH_3)_2\}_2(\mu\text{-}O_2CCH_3)]^{3+}$.

Discussion

Manifestations of the Trans Effect in the Comparative Chemistries of *cis*- and *trans*-Diammineplatinum(II) Complexes. For ligands relevant to the present work, the accepted order of the trans effect is $Cl^- > NH_3 > OH^- > H_2O$.[40] The abstraction of the first chloride ion from *trans*-$[PtCl_2(NH_3)_2]$ with silver salts is therefore not difficult, owing to the moderate trans effect of the trans chloro ligand. Removal of the second chloride ligand, which is trans to weaker H_2O, is much more difficult. For the cis isomer, both of the chloride ligands are trans to ammine, which has a moderate trans effect, so both are removed relatively easily.

When any incoming ligand reacts with the *trans*-diaqua complex, the replacement of the first coordinated water molecule, trans to water, would be expected to be slower than for the cis isomer. This accounts for the need for standing or heating for the formation of *trans*-$[Pt(A)(H_2O)(NH_3)_2]^{(2-n)+}$ from *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$ and an oxygen-donor ligand A^{n-}, while, with cis complexes, equilibrium is usually reached within a few minutes.[19] Since an oxygen-donor ligand, A^{n-}, will also have a relatively low trans effect, formation of the disubstituted complex *trans*-$[Pt(A)_2(NH_3)_2]^{(2-2n)+}$ also requires heating or long standing.

When *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$ reacts with chloride, however, the initial product, *trans*-$[PtCl(H_2O)(NH_3)_2]^+$, has the remaining water molecule coordinated trans to chloride, with its moderate trans effect. This water molecule is more labile than that in the diaqua complex. When *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$ reacts with 1 mol equiv of chloride ion, only half therefore reacts to give *trans*-$[PtCl_2(NH_3)_2]$. For similar reasons, reaction of $[Pt(H_2O)_4]^{2+}$ with 1 mol equiv of chloride gives predominantly *trans*-$[PtCl_2(H_2O)_2]$.[41–43]

The lesser lability of the mutually trans nitrato ligands in *trans*-$[Pt(ONO_2)_2(NH_3)_2]$ compared with the cis isomer also accounts for the observation that, on dissolution in dmf, the nitrato ligands remain bound until the solution is heated, or allowed to stand for long periods, while an equilibrium is quickly established for the cis isomer between nitrato and dmf complexes.

Acid Dissociation Constants. The acid dissociation constants of *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$ have been previously determined by potentiometric titration by Grinberg and Ryabchikov,[44] by Jensen,[45] and by Perumareddi and Adamson.[46] Their values are included in Table II. Given the slightly different conditions, our values agree well with those of Jensen and of Pemurareddi and Adamson, but not with those of Grinberg. A likely source of error for the potentiometric method is the formation of hydroxo-bridged complexes. Hydroxo-bridged oligomers form more slowly for trans complexes than for cis, so that a rapid titration of a dilute solution may give good results.

From the values given in Table II, it is evident that the acid dissociation constants for water coordinated to platinum(II) are affected profoundly by the other ligands present, and span a considerable range. We have previously commented[38] on the greater acid strength of coordinated water in the anionic complex $[Pt(NO_2)_3(H_2O)]^-$ compared with the cationic complex $[Pt(H_2O)(NH_3)_3]^{2+}$, which we ascribed to the π-acceptor capacity of the nitro ligands. Although acid dissociation constants have not been measured, it is evident that the coordinated water molecules in $[Pt(bpy)(H_2O)_2]^{2+}$ (bpy = 2,2′-bipyridyl) are very acidic,[47] probably also associated with the π-acceptor capacity of bpy.

Coordinated water in *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$ is clearly more acidic than in the cis isomer. This difference in pK_{a1} values may

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be rationalized in terms of the different trans influences of water and ammine. Because the trans influence of water is weak, a water molecule coordinated trans to water is expected to bind more strongly to the metal than a water molecule bound trans to a ligand with higher trans influence. That is, there will be greater net transfer of electronic charge from the oxygen atoms to the metal. With compensating movement of electrons from the hydrogen atoms toward the oxygen atoms, the H atoms will become more positive. Once one water molecule is deprotonated, the remaining water molecule in *trans*-$[Pt(OH)(H_2O)(NH_3)_2]^+$ is trans to the hydroxide, whose trans influence is higher, so that there is a smaller difference between the pK_{a2} values for the two isomers. In noting the effect of the other ligands on the acidity of coordinated water, it is interesting to recall that the acid dissociation constant for $[Pt(H_2O)_4]^{2+}$ has not been measured, and it is possible that this species is strongly acidic.[41,43]

The chloro–aqua complex, *trans*-$[PtCl(H_2O)(NH_3)_2]^+$, is also more acidic than the cis isomer (Table II). With indicator measurements such as NMR coupling constants, the trans influence of chloride is less than that of ammine,[20,40] so that water would be expected to bind more strongly trans to chloride, resulting in greater acid strength.

^{195}Pt Chemical Shifts for Cis and Trans Isomers. In discussing the difference in δ_{Pt} between cis and trans isomers of $[PtL_2X_2]$, McFarlane[48] proposed that the difference between the isomers was primarily due to differences in the electronic excitation energy ΔE. When the two kinds of ligands present, L and X, were very different in trans influences, the difference in ΔE between the isomers would tend to be large. The trans isomer would then be expected to give a resonance to lower shielding, as ΔE would be smaller for this isomer. Goggin et al.[49] showed, using several examples, that the chemical shift difference between cis and trans isomers can indeed be related to the difference in trans influences between L and X, but that the rule that trans isomers occur to lower shielding is not universally true, because factors in addition to ΔE affect δ_{Pt}. The trans-influence difference between ammine and chloride is relatively small,[40] so that it is not surprising that *cis*- and *trans*-$[PtCl_2(NH_3)_2]$ have very similar ^{195}Pt shifts in dmf. The difference between ammine and aqua is larger,[40] and *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$ gives a ^{195}Pt peak 210 ppm to lower shielding than the cis isomer. The other *trans*-diammine complexes containing two oxygen-donor ligands also gave resonances in the range −1184 to −1413 ppm. The sign of the shift caused by replacing H_2O by A^{n-} is the same when the initial complex is *cis*-[19] or *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$ or $[Pt(H_2O)_4]^{2+}$.[43]

For $[PtCl(H_2O)(NH_3)_2]^+$, the chemical shift difference between cis and trans isomers is significant, but much smaller than for the diaqua complexes (Table I).

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Supplementary Material Available: Table S1, listing microanalytical data (1 page). Ordering information is given on any current masthead page.

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