Solvation and Bifunctional Proton Transfer of $(NH_3)_5PtNH_2^{3+}$ in Aqueous Solution[1]

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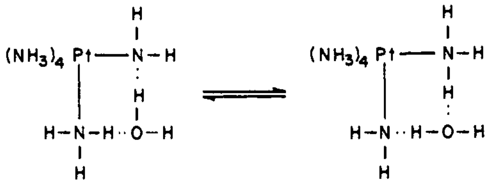
Abstract: Rates of OH and NH proton exchange have been measured for aqueous solutions of $Pt(NH_3)_6^{4+}$ (A) and $(NH_3)_5PtNH_2^{3+}$ (B) in H_2O and HOD–D_2O over a wide range of conditions. The dominant reaction involves one molecule of B and one water molecule and is such that the basic site ($-NH_2$) migrates efficiently among all six nitrogen atoms. A bifunctional reaction mechanism is thus indicated. In H_2O, the formal first-order rate constant $k = 2.2 \times 10^8$ sec^{-1} at 25°; $\Delta H^{\ddagger} = 0.7$ kcal/mol; $\Delta S^{\ddagger} = -18$ gibbs/mol. Rate constants for NH and ND exchange between B and water in HOD–D_2O are practically equal and differ from k in H_2O by a factor equal to the relative viscosity. These results suggest that proton or deuteron transfer is ultrafast and that exchange of the water molecule between the solvation shell of B and bulk solvent is rate determining. Statistical factors for proton exchange of HOD relative to HOH show that the water molecule on the reactive site is able to rotate rapidly. As a result, two hydrogen atoms of water and one or all five NH hydrogen atoms of the bifunctional site are scrambled into a random distribution during each encounter. We also report acid dissociation constants $_cK_a$ and conductivity measurements for $Pt(NH_3)_6Cl_4$ in H_2O and rate constants for symmetrical proton exchange between A and B in chloride media. Salt effects on these quantities are more nearly a function of the chloride concentration than of the total ionic strength and indicate the formation of ion pairs (outer-sphere complexes) of the type $Pt(NH_3)_6Cl^{3+}$.

Kinetic analysis of proton exchange between aquated or ammoniated cations of high electrical charge and solvent water molecules can give much insight into the solvation of such ions. We wish to report a detailed study of the hexaamminoplatinum(IV) ion $Pt(NH_3)_6^{4+}$ and its conjugate base $(NH_3)_5PtNH_2^{3+}$ in H_2O and HOD–D_2O solution. The study includes rates of proton exchange measured by nuclear magnetic resonance (nmr), acid dissociation constants, and conductivities.

We find that proton exchange between $(NH_3)_5PtNH_2^{3+}$ and water is exceedingly fast. The pseudo-first-order rate constant for transfer of a proton from an NH site on this ion to an OH site in bulk water is 2×10^8 sec^{-1} at 25°. Our data indicate that the proton-transfer step involves one water molecule and that the ion reacts as a bifunctional reagent (eq 1). This proton-transfer step is very much faster than 2×10^8 sec^{-1}. The rate-determining step for the overall process is the exchange of the water molecule between the bifunctional site in the ionic solvation shell and bulk water.



(1)

Our data indicate further that the rate of rotation of the water molecule on the bifunctional site, about the $NH \cdot OH_2$ hydrogen-bond axis, is very much faster than 2×10^8 sec^{-1}. Thus, owing to rapid rotation and proton exchange, the two water protons and one or all five NH protons of the bifunctional site become scrambled into a random distribution before the water molecule returns to bulk water. As a result, the statistical probability for *proton* exchange is only half as great for an HOD molecule as for an HOH molecule in any single encounter. Our nmr data provide direct evidence for this reduction in statistical probability.

The effectiveness of bifunctional catalysis in general acid and/or base catalyzed reactions has been widely appreciated since the pioneering work of Swain and Brown.[2-4] A necessary condition is that the proton-donating and -accepting sites of the bifunctional catalyst be sterically compatible with the two reactive centers in the substrate. For water molecules adsorbed on oriented fibers of collagen or DNA, steric compatibility seems to require that the repeat distance between hydrogen-bonding centers in the substrate be nearly equal to the O···O distances in ice I.[5,6] In the present case it may be significant that the N···N distance in the octahedral $(NH_3)_5PtNH_2^{3+}$ ion is 2.83 Å,[7] very close to the nearest-neighbor O···O distance in ice (2.76 Å) and in liquid water.[8]

Rony[4] has suggested that bifunctional catalysis is especially effective if the bifunctional proton transfer is coupled to the shift of a double bond (tautomeric catalysis). However, our data show that the shift of a double bond is not necessary for facile reaction.

There is a striking contrast between the present results for $(NH_3)_5PtNH_2^{3+}$ and previous results[9] for $(H_2O)_5AlOH^{2+}$. There is a strong similarity in the structures of these ions. Both have octahedral coordi-

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] C. G. Swain and J. F. Brown, Jr., *J. Amer. Chem. Soc.*, **74**, 2538 (1952).

[3] For some recent examples, see R. E. Barnett and W. P. Jencks, *ibid.*, **91**, 2358 (1969); B. A. Cunningham and G. L. Schmir, *ibid.*, **89**, 917 (1967); F. M. Menger, *ibid.*, **88**, 3081 (1966).

[4] P. R. Rony, *ibid.*, **91**, 6090 (1969).

[5] C. Migchelsen, H. J. C. Berendsen, and A. Rupprecht, *J. Mol. Biol.*, **37**, 235 (1968).

[6] H. J. C. Berendsen, *J. Chem. Phys.*, **36**, 3297 (1962).

[7] Based on X-ray diffraction data for the following crystals: N···N in $(NH_3)_5PtCl_4$; O···O in $AlCl_3 \cdot 6H_2O$. R. W. G. Wyckoff, "Crystal Structures," Vol. 3, 2nd ed, Interscience, New York, N. Y., 1951, pp 790, 796.

[8] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, p 301.

[9] D.-W. Fong and E. Grunwald, *J. Amer. Chem. Soc.*, **91**, 2413 (1969).

nation shells and sites suitable for bifunctional proton transfer. (The O···O distance in $Al(OH_2)_6^{3+}$ is 2.65 Å.)[7] However, while for $(NH_3)_5PtNH_2^{3+}$ the rate constant for bifunctional proton transfer to a water molecule is much greater than 2×10^8 sec^{-1}, for $(H_2O)_5AlOH^{2+}$ it was found to be undetectably small,[9] an upper limit being 10^7 sec^{-1}. At the same time, there is strong evidence that the aquated aluminum ion is the more tightly hydrated of the two ions. For instance, the Stokes law radius (estimated from the equivalent conductivity[10]) is 3.9 Å for $Pt(NH_3)_6$,$^{4+}$ suggesting that the kinetic unit might be the unhydrated ion, but it is 4.7 Å for $Al(OH_2)_6^{3+}$, suggesting that the kinetic unit is larger than the formal ion. Moreover, the rate constant for breaking the hydrogen bond between the basic site and water in $(H_2O)_5AlOH \cdot HOH^{2+}$ has been reported[9] to be 4×10^7 sec^{-1}, an uncommonly small value suggestive of strong hydration.

Some Electrolytic Properties of $Pt(NH_3)_6Cl_4$. All experiments reported in this paper involved the chloride salt, $Pt(NH_3)_6Cl_4$, which was prepared from chloroplatinic acid, ammonium carbonate, and liquid ammonia.[11] In order to deduce rate constants from the nmr data, we needed acid dissociation "constants" ${}_cK_a$ for $Pt(NH_3)_6^{4+}$ in terms of molar concentrations. These were measured by a previously described differential potentiometric method[12] under the same conditions of temperature and solute concentration as in the kinetic experiments. Results are listed in Table I and are consistent with earlier measurements[11] under somewhat different conditions.

Table I. Acid Dissociation of $Pt(NH_3)_6^{4+}$ in Water at 25.0°

$[Pt(NH_3)_6Cl_4]$, F	[Chloride], F	$10^8{}_cK_a$, M	k_a, sec^{-1}	$10^{-9} \cdot k_{-a}$, sec^{-1} M^{-1}
		In H_2O		
0.00294	0.0118	6.92 ± 0.10		
0.00702	0.0281	5.99 ± 0.13		
0.01463	0.0586	4.69 ± 0.12	119	2.53
0.01478	0.1154[a]	2.86 ± 0.07	109	3.81
0.02758	0.1103	3.07 ± 0.08	96	3.11
0.04859	0.1944	2.08 ± 0.06	94	4.54
		In $HOD-D_2O$ (5 atom % H)		
0.04981	0.1992	0.62[b]	21.4[c]	3.5[d]

[a] 0.0563 F NaCl added. [b] We assumed a value of 0.301 for the D_2O–solvent isotope effect on ${}_cK_a$. [c] Experimental value of rk'_a. [d] $rk'_{-a} = rk'_a/0.62 \times 10^{-8}$.

We were also interested in the equivalent ionic conductivity of $Pt(NH_3)_6^{4+}$, in order to estimate the Stokes law radius (see above) and predict rate constants for diffusion-controlled reactions.[13] Results are listed in the Experimental Part. The extrapolation to infinite dilution was somewhat uncertain: for $Pt(NH_3)_6Cl_4$, $\lambda_0 = 170 \pm 2$; for $Pt(NH_3)_6^{4+}$, $\lambda_0 = 94 \pm 2$ (mhos at 25°; concentrations expressed in equivalents per liter). The diffusion coefficient of $Pt(NH_3)_6^{4+}$ is calculated[10] from λ_0 to be 6.3×10^{-6} cm^2 sec^{-1}.

Because of the high ionic charge of the substrate, interionic effects are expected to be quite important. Instructive activity coefficient data are available for the model compounds $Pt^{IV}(en)_3Cl_4$ and $Pt^{IV}(en)_3(ClO_4)_4$ [en = $NH_2CH_2CH_2NH_2$] in aqueous solution.[14] The perchlorate salt was thought to behave like a strong 4:1 electrolyte.[14] When the activity coefficients were fitted to the Debye–Hückel theory, the $\mathring{a}$ parameter (which expresses the distance of closest approach) turned out to be quite large, 11.5 Å at 25°.[14] This result would imply that at the ionic strengths used in our kinetic experiments (0.15–0.5 M), the activity coefficients for free ions would be relatively insensitive to changes in the ionic strength. The activity coefficients for $Pt^{IV}(en)_3Cl_4$ were consistently smaller than those for the perchlorate salt at the same formal concentration, suggesting the formation of ion pairs (outer-sphere complexes) of the type $Pt(en)_3Cl^{3+}$.

Our results for $Pt(NH_3)_6Cl_4$ are qualitatively consistent with this description. In particular, the values reported for ${}_cK_a$ (Table I) are more nearly a function of the chloride concentration than of the ionic strength. Similarly, our conductivity data, while being far from definitive, suggest that at 0.01 F concentration a fraction of the order of 10% of the $Pt(NH_3)_6^{4+}$ ions is converted to $Pt(NH_3)_6Cl^{3+}$ ion-pair complexes.[15]

Kinetic Measurements. Rates of proton exchange were deduced from longitudinal (T_1) and transverse (T_2) nmr relaxation times, measured by pulse methods, as described previously.[16] To simplify the notation in the following we shall let A denote $Pt(NH_3)_6^{4+}$ and B (for conjugate base) denote $(NH_3)_5PtNH_2^{3+}$. Mean residence times of a proton were measured for two distinct exchange processes. (1) In ^{17}O-enriched water containing both A and B in 1:1 or 10:1 ratio, we measured τ_W, the mean lifetime of an OH bond of a water molecule during one cycle of ^{17}OH–OH exchange. (2) In mildly acidic water (pH <5.5) containing A, we measured τ_{NH}, the mean time a proton resides on an NH site of A during one cycle of exchange between an NH site of A and an OH site of water.

Both processes were studied in H_2O and in $HOD-D_2O$. Methods used to deduce τ_W and τ_{NH} from the nmr data were analogous to those reported previously[16] and need not be described again. We shall also use the same symbols as in the previous paper.[16]

Kinetic Analysis of τ_W. As is well known, proton exchange among water molecules is very effectively catalyzed by hydrogen ions and hydroxide ions.[17] In the absence of other catalysts, $1/\tau_W$ goes through a minimum of about 450 sec^{-1} in H_2O at pH 7.1 and of about 140 sec^{-1} in $HOD-D_2O$ at pH 7.4.[18] These pH values are slightly below p_cK_a for A. It is therefore possible, by using dilute solutions containing both A and B at a buffer ratio [A]/[B] between 1 and 10, to measure $1/\tau_W$ under conditions where catalysis by H^+ and OH^- amounts to 1100 sec^{-1} or less.

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(10) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London, 1959, p 43.

(11) R. C. Johnson, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, 24, 59 (1962).

(12) E. Grunwald and D.-W. Fong, *J. Phys. Chem.*, 73, 650 (1969).

(13) M. Eigen, *Z. Phys. Chem. (Frankfurt am Main)*, 1, 176 (1954).

(14) C. H. Brubaker, Jr., *J. Amer. Chem. Soc.*, 78, 5762 (1956); 79, 4274 (1957).

(15) For a discussion of the theoretical problems for similar electrolytes of high charge, see K. O. Groves, J. L. Dye, and C. H. Brubaker, Jr., *ibid.*, 82, 4445 (1960).

(16) D. Rosenthal and E. Grunwald, *ibid.*, 94, 5956 (1972).

(17) S. Meiboom, *J. Chem. Phys.*, 34, 375 (1961).

(18) Rates of H^+ and OH^- catalyzed OH-proton exchange among water molecules were calculated using kinetic constants in Table II of ref 16.

Table II. Sample Results for τ_W in Solutions of $(NH_3)_5PtNH_2{}^{3+}$ near pH 7 at 25.0°

Atom % H	[A], *M*	[B], *M*	$10^{-3}/\tau_W$, sec^{-1}	$10^{-3}/\tau_{W,B}$, $sec^{-1\,a}$	$k_{W,B}(k'_{W,B})$, $sec^{-1\,b}$
			In H_2O		
100	0.0259	0.0271	52.2 ± 3.7	51.1	2.10×10^8
100	0.0175	0.0183	36.9 ± 2.1	36.1	2.19×10^8
100	0.0120	0.0126	24.6 ± 1.2	23.9	2.11×10^8
100	0.0081	0.00842	17.4 ± 0.8	16.8	2.22×10^8
100	0.0043	0.00442	8.6 ± 0.4	8.1	2.02×10^8
100	0.1837	0.0176	38.8 ± 2.2	38.1	2.41×10^8
100	0.1250	0.0120	26.2 ± 1.5	25.7	2.38×10^8
100	0.0483	0.00463	10.0 ± 0.6	9.4	2.24×10^8
			In $HOD-D_2O$		
28	0.0273	0.0237	21.9 ± 0.9	21.7	1.02×10^8
24	0.0234	0.0203	18.5 ± 0.8	18.3	1.00×10^8
18	0.0174	0.0151	13.7 ± 0.7	13.5	0.99×10^8
12	0.0118	0.0102	7.6 ± 0.4	7.4	0.81×10^8

[a] Equation 2 or 3. pH of solutions calculated from K_a values in Table I. Kinetic constants from ref 16. [b] Equation 4 or 5.

Typical kinetic results obtained under such conditions are listed in Table II. The values of $1/\tau_W$ are in each case quite large, so that catalysis by H^+ and OH^- accounts for less than 6% of the total rate. Moreover, $1/\tau_W$ is essentially proportional to [B], even for a tenfold variation in [A]/[B] and a 40-fold variation in [A].

Let $1/\tau_{W,B}$ denote the increase in $1/\tau_W$ over that due to catalysis by H^+ (rate constant k_+) and OH^- (rate constant k_-).

$$\frac{1}{\tau_{W,B}} = \frac{1}{\tau_W} - \frac{k_+[H^+]}{3} - \frac{k_-[OH^-]}{2} \tag{2}$$

Using the same notation as before,[16] in $HOD-D_2O$ the corresponding quantity is defined in (3), where L denotes any hydrogen isotope, H or D, and primed symbols indicate that the given quantity applies to $HOD-D_2O$. For purposes of kinetic analysis we are interested in the rate of exchange $R_{W,B}$ and the formal rate constant $k_{W,B}$. These quantities are related to τ_W and [B] according to (4) in H_2O and according to (5) in $HOD-D_2O$. Results obtained on this basis are shown in Table II.[18]

$$\frac{1}{\tau'_{W,B}} = \frac{1}{\tau'_W} - \frac{k'_+[L^+]}{3} - \frac{k'_-[OL^-]}{2} \tag{3}$$

$$2[H_2O]/\tau_{W,B} = R_{W,B} = k_{W,B}[B] \tag{4}$$

$$2[L_2O]/\tau'_{W,B} = R'_{W,B} = k'_{W,B}[B] \tag{5}$$

On the basis of 15 experiments in H_2O, $k_{W,B} = (2.2 \pm 0.2) \times 10^8$ sec^{-1} at 25°. In two experiments, measurements were made also at 5, 15, and 35°. Average activation parameters were as follows: $\Delta H^{\ddagger} = 0.7 \pm 0.3$ kcal/mol; $\Delta S^{\ddagger} = -18 \pm 1$ gibbs/mol.

For the experiments in $HOD-D_2O$ we had intended to use a medium containing 5 atom % H for comparison with measurements of τ_{NH}. However, owing to an error (not discovered until after the experiments had been completed) in the protium content of our ^{17}O-enriched heavy water, the actual values ranged from 12 to 28%. The error was fortunate, because it enabled us to show that, in this range, $k'_{W,B}$ is quite insensitive to the atom per cent H, a feature that is consistent with the proposed reaction mechanism. The mean value of $k'_{W,B}$ is $(0.95 \pm 0.1) \times 10^8$ sec^{-1} at 25° in this range. If we assume that $k'_{W,B}$ varies linearly with atom per cent H, a least-squares calculation gives the result that in 5 atom % $HOD-D_2O$, $k'_{W,B} = (0.8 \pm 0.1) \times 10^8$ sec^{-1}.

Catalysis of proton exchange among water molecules by B can be visualized as follows. A water molecule reacts with B such that an OH proton is exchanged for an NH proton. (A possible mechanism is shown in eq 1; however, the actual mechanism need not concern us here.) A very short time later, the same B molecule reacts with a *different* water molecule, and the given proton is transferred to a new OH site. If the residence time of the proton on B is sufficiently short, the short-lived stay on B will produce no detectable nmr exchange broadening; the proton might as well have transferred directly from one water molecule to another. However, the rate law proves that B intervenes as a catalyst. Later in this paper, $k_{W,B}$ and $k'_{W,B}$ will be related to the mean residence time of an NH proton on B.

Kinetic Analysis of τ_{NH}. Proton exchange between NH sites of A and OH sites of water was measured in acidic solutions (pH <5.5). Under these conditions the concentration of B in equilibrium with A is too small, and the lifetime of B is too short, for the NH protons of B to produce significant nmr exchange broadening. However, B *can* intervene as a reaction intermediate or a catalyst.

Soon after we had begun these measurements, it was clear that the rate law for $1/\tau_{NH}$ was formally very similar to that for NH-OH proton exchange between aliphatic ammonium ions (*e.g.*, $(CH_3)_3NH^+$) and water.[19,20] However, it was also clear that the formal similarity was not an exact analogy, because rate constants deduced on that basis were implausibly high. For instance, there was a kinetic term analogous to that for reversible acid dissociation ($A \rightleftarrows B + H_3O^+$). However, the corresponding proton-exchange rates were about 20 times greater than the theoretical maximum, which obtains when the reaction of B(aq) with H_3O^+(aq) is diffusion controlled. In the latter case, the rate constant k_{-a} should be about $(1.5\text{–}2.0) \times 10^9$ sec^{-1} M^{-1}, which is the expected value when the

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(19) For a recent review, see M. C. Caughman, M.Sc. Thesis, University of Georgia, Athens, Ga., 1970.

(20) For example, see E. Grunwald, *J. Phys. Chem.*, 67, 2208, 2211 (1963).

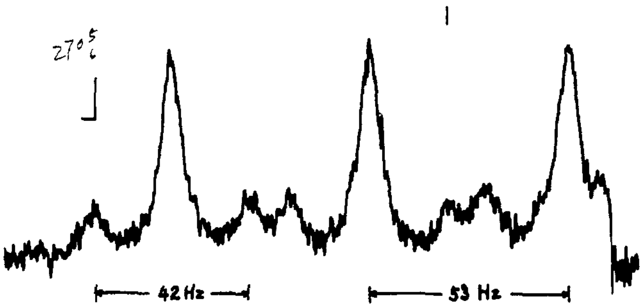

Figure 1. NH proton nmr spectrum of 0.1 *F* $Pt(NH_3)_6Cl_4$ in 0.4 *F* aqueous $HClO_4$ at 100 MHz. The spectrum shows spin–spin interaction with ^{14}N (*spin* = 1, *J* = 53 Hz) and, for 33.7% of the protons, an additional spin–spin interaction with ^{195}Pt (spin = $^1/_2$, *J* = 42 Hz). The nmr lines are almost as sharp as in NH_4^+, showing that T_1 relaxation of the ^{14}N nucleus is quite slow, and there is little or no exchange broadening. We acknowledge with thanks the collaboration of Dr. B.-M. Fung and the use of the 100-MHz nmr spectrometer at Tufts University.

ionic charge of the conjugate base is +3.[21] As a matter of fact, for the analogous reaction of H_3O^+ with the conjugate base of $Pt(en)_3{}^{4+}$, k_{-a} = 1.9 × 10^9 sec^{-1} M^{-1} at 12° and 0.1 *M* ionic strength, as measured by temperature jump,[22] and we expected a similar value here. Consequently, to account for the proton-exchange rates between $Pt(NH_3)_6{}^{4+}$ and water, we had to abandon the usual assumption that only one NH proton can exchange during each reversible cycle (A → B → A) and postulate instead that as many as all 18 NH protons can exchange.

Before deriving a suitable rate law, we wish to introduce two further pieces of evidence. At our request, Warrick and Eyring[23] examined the kinetics of acid dissociation of $Pt(NH_3)_6{}^{4+}$ by an electric field-jump method. It is a pleasure to thank them also at this time for permission to describe the results. It turned out that acid dissociation of $Pt(NH_3)_6{}^{4+}$ made only a marginally significant contribution to the experimental relaxation time in the optimum pH range (6.7–7.2) and the determination of k_{-a} was accordingly uncertain. Nevertheless in the two or three experiments in which the rate of this process could be obtained, k_{-a} was about (1-3) × 10^9 sec^{-1} M^{-1} at 25° (0.0024 *M* ionic strength) of the expected magnitude for the diffusion-controlled reaction.

The second piece of evidence concerns the behavior of $1/\tau_{NH}$ at low pH. For many aliphatic ammonium ions, $1/\tau_{NH}$ approaches zero in strong aqueous acid.[19,24] We find the same is true for $Pt(NH_3)_6{}^{4+}$. For instance, for 0.015 *F* $Pt(NH_3)_6Cl_4$, $1/\tau_{NH}$ = 76 sec^{-1} at pH 2.8, 29 sec^{-1} at pH 1.8, and *ca.* 5 sec^{-1} at pH 0.8. The latter value is less than 5% of the rate constant for acid dissociation. Similarly, Figure 1 shows the NH-proton nmr spectrum of 0.1 *F* $Pt(NH_3)_6Cl_4$ in 0.4 *F* $HClO_4$. The spectrum consists of sharp lines with little or no exchange broadening. It also shows the characteristic spin–spin interaction with ^{14}N (spin = 1, *J* = 53 Hz) and, for about one-third of the protons, an additional spin–spin interaction with ^{195}Pt (spin = $^1/_2$, natural abundance 33.7%, *J* = 42 Hz).

To derive a rate law that fits our data well, we shall use the following model.

(a) Direct proton exchange between A and H_2O may be neglected. Proton exchange requires the prior formation of B.

(b) The rate of NH–OH proton exchange, R_{NH}, is given by eq 6, where R_B = rate of formation of B from A and $\bar{n}$ = number of protons originally on NH sites of A that are transferred to water–OH sites during the mean lifetime λ of B in one cycle of reaction (A → B → A). $\bar{n}$ is an average number for many cycles of reaction and varies with λ.

$$R_{NH} = R_B\bar{n} \tag{6}$$

(c) B is formed from A by two parallel reactions: acid dissociation (rate constant k_a) and symmetrical proton transfer between A and B (rate constant k_2), according to (7). Equation 7 will cause the final rate law to be similar to that for aliphatic ammonium salts. Because A and B are in dynamic equilibrium, R_B = R_{-B} and $k_a[A] = k_{-a}[H^+][B]$. The mean lifetime λ of B is therefore given by (8).

$$R_B = k_a[A] + k_2[A][B] \tag{7}$$

$$\lambda = [B]/R_B = 1/(k_{-a}[H^+] + k_2[A]) \tag{8}$$

(d) The maximum value of *n* is 18, since there are 18 NH sites in $Pt(NH_3)_6{}^{4+}$. The minimum value is zero, because at low pH R_{NH} goes to zero while R_B approaches $k_a[A] > 0$. Also at low pH, λ goes to zero. We may conclude, therefore, that at the instant of its formation from A, B still has all 18 of the original protons of A "bonded" to nitrogen atoms; there will be 17 N–H covalent bonds and one N···H hydrogen bond.

Let *k* be the rate constant for exchange of an NH proton of B with an OH proton of water. Suppose that at time *t* after the formation of B, a number *x* of the original 18 protons of A are still "bonded" to nitrogen atoms of B. On a purely statistical basis, the probability that the next proton exchange will involve one of the original NH protons is *x*/18, and the probability −d*x* that this will happen during the subsequent infinitesimal time d*t* is given by (9). To obtain *x* as a function of *t*, we integrate and let *x* = 18 when *t* = 0. The result is (10). The mean value $\bar{x}$ is obtained by averaging *x* over many cycles of exchange. In any given experiment, the composition of the solution is constant; hence, the process B → A follows (pseudo) first-order kinetics. That is to say, if the mean lifetime of B is λ, the probability of survival for *t* seconds is $e^{-t/\lambda}$. Therefore $\bar{x}$ is given by (11). The average number $\bar{n}$ of new protons introduced into A during one cycle A → B → A is given by $\bar{n} = 18 - \bar{x}$. Thus we obtain the final expression (12). It should be empha-

$$-\mathrm{d}x/\mathrm{d}t = (x/18)k \tag{9}$$

$$x = 18e^{-kt/18} \tag{10}$$

$$\bar{x} = \frac{\int_0^\infty xe^{-t/\lambda}\mathrm{d}t}{\int_0^\infty e^{-t/\lambda}\mathrm{d}t} = \frac{18}{1 + (k\lambda/18)} \tag{11}$$

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(21) L. P. Holmes, D. L. Cole, and E. M. Eyring, *J. Phys. Chem.*, 72, 301 (1968); L. DeMaeyer and K. Kustin, *Annu. Rev. Phys. Chem.*, 14, 5 (1963).

(22) M. Eigen and W. Kruse, *Z. Naturforsch.*, *B*, 18, 857 (1963).

(23) Unpublished work of Percy Warrick, Jr., and E. M. Eyring, University of Utah, Salt Lake City, Utah. Private communication to E. Grunwald, Feb 9, 1971.

(24) E. Grunwald and E. K. Ralph, *Accounts Chem. Res.*, 4, 107 (1971).

$$\bar{n} = 18/[1 + (18/k\lambda)] \qquad (12)$$

sized that the statistical model implied by eq 9 is probably not quite realistic. We attribute the success of this model in fitting our data to two factors: the relatively large number of NH protons in A and a bifunctional reaction mechanism for proton transfer (eq 1) in which the NH_2 function migrates efficiently among all coordination sites.

On combining eq 6–8 and 12 we obtain the rate law 13. Equation 13 contains three independent rate

$$\frac{1}{\tau_{NH}} = \frac{R_{NH}}{18[A]} = \frac{(k_a + k_2[B])k}{k + 18(k_{-a}[H^+] + k_2[A])} \qquad (13)$$

constants: k_a, k_2, and k; $k_{-a} = k_a/K_a$. Because these rate constants may vary with the ionic strength and/or chloride concentration, rate measurements were made in several series. In each series the concentrations of $Pt(NH_3)_6{}^{4+}$ and Cl^- were kept constant (within a few per cent) and the pH was allowed to vary by addition of small amounts of HCl or NaOH. Results for a typical series are shown in Table III, and "best values" for the rate constants are listed in Tables I and IV. It is clear from Table III that the precision of $1/\tau_{NH}$ varies widely in a given series. Accordingly, the rate constants were calculated by a weighted least-squares procedure. We estimate the following standard errors: k_2, ±5–10%; k_a, k_{-a} ±10–20%; k, ±15–30%. Table III illustrates the excellent fit of the rate law over a wide pH range.

Table III. Dependence of τ_{NH} on p_cH for 0.04859 F $Pt(NH_3)_6Cl_4$ in H_2O at 25.0°

p_cH	$1/\tau_{NH}$, sec^{-1} obsd	$1/\tau_{NH}$, sec^{-1} calcd (eq 13)[a]
5.545	9090 ± 400	9600
5.230	4580 ± 170	4680
4.853	2120 ± 60	2010
4.466	960 ± 200	869
4.086	393 ± 20	405
3.757	230 ± 6	227
3.447	149 ± 5	144
3.061	91 ± 3	90.7
2.714	59 ± 2	61.1
2.426	42 ± 2	41.8
2.099	27 ± 2	24.9

[a] Based on rate constants listed in Tables I and IV.

Table IV. Rate Constants Based on Eq 13 and 17 for $Pt(NH_3)_6{}^{4+}$ in Water at 25°

$[Pt(NH_3)_6$-$Cl_4]$, F	[Chloride], F	$10^{-7}k_2$, sec^{-1} M^{-1}[a]	$k_2/[Cl^-]$ × 10^{-8}, sec^{-1} M^{-2}	$10^{-8}k$, sec^{-1}
		In H_2O		
0.01463	0.0585	0.72 ± 0.07	1.23	1.6 ±0.5
0.01478	0.1154[b]	2.20 ± 0.22	1.91	1.4 ± 0.5
0.02758	0.1103	1.65 ± 0.12	1.50	2.1 ± 0.4
0.04859	0.1944	3.00 ± 0.15	1.54	2.3 ± 0.3
		In HOD–D_2O (5 atom % H)		
0.04981	0.1992	1.18 ± 0.06[c]	0.59	1.9 ± 0.3[d]

[a] Calculated on the basis of $_cK_a$ in Table I. [b] 0.0563 F NaCl added. [c] $rk'_2 \times 10^{-7}$ [d] k'_{NH}.

Values of k_a and k_{-a} are listed in Table I. The values of k_{-a} show a small upward drift with the ionic strength μ and/or $[Cl^-]$, as might be expected for a reaction involving two cations. Various methods of extrapolation to infinite dilution give $k^0_{-a} = (1.8 \pm 0.5) \times 10^9$ sec^{-1} M^{-1} of the expected magnitude for the diffusion-controlled reaction. On applying the appropriate equation derived by Eigen,[13] we find that the effective "encounter diameter" is 4.74 Å.

Values of k_2 and k are listed in Table IV. The values of k_2 increase sharply with μ and/or Cl^-, reflecting the high cationic charges of the reactants. $k_2/[Cl^-]$ is approximately constant, suggesting specific interaction with chloride ion.

The rate constant k for exchange of an NH proton of B with an OH proton of water is the direct counterpart of $k_{W,B}$ and is therefore of special interest. Unfortunately, k is the least accurate of the rate constants evaluated by our data, and the values in Table IV show more variation than we would have liked. Nevertheless, the average k, $(2.0 \pm 0.3) \times 10^8$ sec^{-1}, is in very good agreement with the value, $(2.2 \pm 0.2) \times 10^8$ sec^{-1}, obtained for $k_{W,B}$. If it be granted that the two rate constants refer to the identical process, then the ratio $k_{W,B}/k$ evaluates the number of water molecules that react each time a molecule of B reacts. This number is evidently unity and that is why eq 1 shows B and H_2O reacting in a 1 to 1 ratio.[25]

Deuterium Isotope Effects. We also measured τ_{NH} for proton transfer in an HOD–D_2O solvent in which the protium fraction $f = 0.05$. This value is small enough so that the assumption, $f \ll 1$, is approximately justified. By making this assumption, we can derive the rate law in a straightforward manner. In the following, primed symbols will indicate that the given quantity applies to HOD–D_2O.

In deriving a rate law for τ'_{NH}, a convenient shortcut is to obtain first the rate of *deuteron* exchange R'_{ND}. When $f \ll 1$, the rate law for R'_{ND} is completely analogous to that for R_{NH}, which was derived earlier (eq 6–12). The result is (14), where the rate constants apply to the same chemical reactions as before but are for deuteron exchange in essentially pure D_2O. In particular, k'_{ND} is the all-deuterium analog of k. $[L^+] \approx [D^+]$.

$$R'_{ND} = R'_B\bar{n}' = \frac{18(k'_a[A] + k'_2[A][B])k'_{ND}}{k'_{ND} + 18(k'_{-a}[L^+] + k'_2[A])} \qquad (14)$$

Next, we express the relative rate of NH and ND exchange according to (15) as the product of the relative reactivity ($k'_{NH}/k'_{ND} = r$) and concentration $[f/(1 - f) \approx f]$ of NH and ND sites in B. We then introduce this result into the definition of $1/\tau'_{NH}$ to obtain (16).

$$\frac{R'_{NH}}{R'_{ND}} = \frac{k'_{NH}f}{k'_{ND}(1 - f)} \approx rf \qquad (15)$$

$$\frac{1}{\tau'_{NH}} \equiv \frac{R'_{NH}}{18[A]f} = \frac{R'_{ND}r}{18[A]} \qquad (16)$$

Finally, on expressing R'_{ND} according to (14) and rearranging, we obtain (17).

$$\frac{1}{\tau'_{NH}} = \frac{(rk'_a + rk'_2[B])k'_{NH}}{k'_{NH} + 18(rk'_{-a}[L^+] + rk'_2[A])} \qquad (17)$$

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(25) By contrast, for benzoic acid in methanol, bifunctional proton transfer of the carboxyl group proceeds with participation by *two* molecules of methanol. E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Amer. Chem. Soc.*, **85**, 522 (1963).

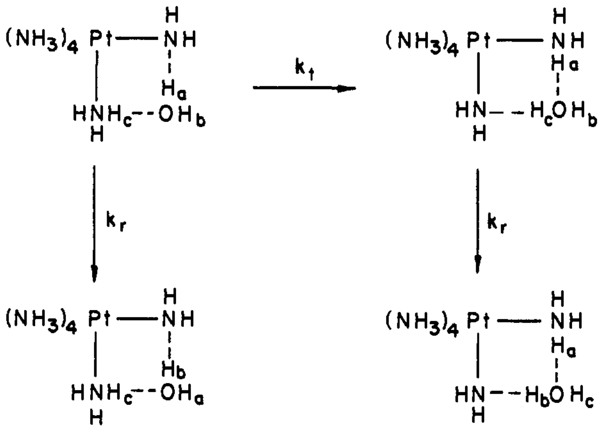

Figure 2. Scrambling of hydrogen atoms owing to bifunctional proton transfer and rotation of the water molecule.

Equation 17 expresses $1/\tau'_{NH}$ as a function of three independent parameters: rk'_a, rk'_2, and k'_{NH}; $rk'_{-a} = rk'_a/K'_a$. We made one series of measurements in which [A] was constant at 0.05 *F* and the pH (essentially p_cD) was varied in ten steps from 2.0 to 6.0. The fit of eq 17 was very satisfactory. The standard error of fit was about the same as that for the data shown in Table III. Values obtained for the kinetic constants are listed in Tables I and IV.

To evaluate *r*, we shall assume that the reaction of the solvated hydrogen ion with B is diffusion controlled. As a result, we can predict k'_{-a} in D_2O from k_{-a} in H_2O and the relative viscosity of the two solvents. For [A] = 0.05 *F*, the calculation is as follows.

$$10^{-9}rk'_{-a} = 3.5 \pm 0.4 \text{ (Table I)}$$

$$10^{-9}k'_{-a} = 10^{-9}k_{-a}\eta/\eta' = (4.5 \pm 0.4)0.81$$

$$r = 0.95 \pm 0.15$$

Recalling that $r = k'_{NH}/k'_{ND}$, the evaluation shows that the kinetic isotope effect on k' is practically unity. This fact is consistent also with the close approximation of k'_{NH} to k, as shown in Table IV. On the basis of the results for [A] = 0.05 *F*, $k'_{NH}/k = 0.83 \pm 0.17$, while the relative viscosity η/η' of the two solvents is 0.81. These results strongly suggest a reaction mechanism in which diffusion rather than proton or deuteron transfer is rate determining.

In the earlier comparison of $k_{W,B}$ with k, we found that these rate constants are essentially equal. However, on comparing the analogous rate constants $k'_{W,B}$ and k'_{NH}, we find that $k'_{W,B}/k'_{NH} = 0.42 \pm 0.08$. Because kinetic isotope effects on k are practically unity, we attribute the deviation from unity in the present case to a statistical factor. A statistical factor of $^1/_2$ for HOD (relative to 1 for HOH) would fit within the experimental error.

Conclusions

Our results show that proton exchange involves a very rapid process in which one molecule of B reacts with one water molecule. This process is such that the basic site ($-NH_2$:) can migrate among all six nitrogen atoms, which rules out any reaction mechanism in which proton exchange is localized at a single nitrogen atom. A bifunctional mechanism such as that shown in Figure 1 is plausible on the basis of chemical precedent and molecular geometry and is consistent with all facts.

To interpret the absence of kinetic isotope effects ($k \approx k'_{NH} \approx k'_{ND}$), we recall that our nmr method measures the proton exchange of water molecules *in bulk water*, so that in each cycle of exchange the water molecule must (i) enter the solvation shell of B, (ii) react with B so as to receive a new proton, and (iii) return to bulk solvent. Ignoring statistical factors for the moment, we can formally represent the overall process of proton exchange in terms of two rate constants, k_s and k_t, as follows. (W denotes a water molecule and an asterisk indicates that the given molecule has received a new proton.)

$$W + B\cdot W \underset{k_s}{\overset{k_s}{\rightleftharpoons}} B\cdot W + W \qquad \text{(i)}$$

$$B\cdot W \underset{k_t}{\overset{k_t}{\rightleftharpoons}} B^*\cdot W^* \qquad \text{(ii)}$$

$$B^*\cdot W^* + W \xrightarrow{k_s} B^*\cdot W + W^* \qquad \text{(iii)}$$

The overall rate constant k_{obsd} for proton exchange ($W \rightarrow W^*$) is equal to $k_sk_t/(k_s + 2k_t)$. We expect that k_t is subject to kinetic isotope effects, while k_s is not. However, k_s may vary inversely as the viscosity of the medium. Since in fact k_{obsd} shows no kinetic isotope effects, we must conclude that $k_t \gg k_s$, in which case $k_{obsd} = k_s/2$. If we introduce appropriate statistical factors, a more general result will be that $k_{obsd} = qk_s$ when $k_t \gg k_s$, where q is the probability that $B\cdot W \rightarrow B^*\cdot W^*$ in one encounter. In the present case, $k_{obsd} = 2 \times 10^8$ sec^{-1} at 25°. Since k_t must be much greater than this, even for deuterium transfer, we have an example of bifunctional proton transfer being ultrafast.[26]

To interpret the relationships between k, k'_{NH}, $k_{W,B}$, and $k'_{W,B}$, we must assume that the water molecule in $B\cdot W$ is able to rotate with a "rate constant" $k_r \gg k_s$. The combined effect of fast proton transfer and rotation of the water molecule will be to cause essentially complete scrambling of H_a, H_b, and H_c in Figure 2 during each encounter. Thus the probability q that the water molecule returning to bulk solvent will incorporate the original NH hydrogen atom (H or D) is $^2/_3$, and the rate constants k, k'_{NH}, and k'_{ND} are all equal to $2k_s/3$. The probability that an H_2O molecule will transfer a proton to an NH site is $^2/_3$, while that for an HOD molecule is $^1/_3$. Thus $k_{W,B} = 2k_s/3$ while $k'_{W,B} = k_s/3$. These statistical factors are consistent with the experimental results.

The mechanism shown in Figure 2 scrambles the two hydrogen atoms of a water molecule with one NH hydrogen atom. However, this mechanism is not unique; any mechanism that will scramble both hydrogen atoms of one water molecule with 1, 2, 3, or any fixed number $n < 18$ of NH hydrogen atoms can formally reproduce our results. Fortunately, the number of plausible alternatives is more limited. For bifunctional reaction, the only acceptable alternative is a mechanism in which *all seven* hydrogen atoms shown in Figure 2 are scrambled during each encounter. This will happen if, besides k_t and k_r, the "rate constant" for rotation of the $-NH_3$ group is also much greater than k_s. We favor this mechanism because it goes far toward explaining

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(26) For some other examples, see E. Grunwald, *Progr. Phys. Org. Chem.*, 3, 317 (1965).

the remarkable success of a statistical model (eq 9–12) in fitting our data.

To interpret the rapid migration of the $-NH_2$ site among all six nitrogen atoms, we assume that there is a rotation or Walden inversion of the $-NH_2$ group, as one water molecule leaves, so as to permit another water molecule, connected to a different adjacent $-NH_3$ group, to form a new bifunctional site. In case of Walden inversion, the $-NH_3$ group of the new bifunctional site would be trans to the original one. For complexes of metal ions with N,N′-disubstituted ethylenediamines, Walden inversion about nitrogen is a familiar base-catalyzed reaction.[27,28] For aliphatic amines in water, there are indications that dehydration and Walden inversion of the nitrogen atom are somehow coupled.[29]

In summary, our proton exchange rates lead to a model of the $(NH_3)_5PtNH_2^{3+}$ ion and its immediate hydration shell in which molecular motion—rotation and the attendant rupture and re-formation of hydrogen bonds—abounds. A similar model seems to apply to $Pt(NH_3)_6^{4+}$, although this conclusion, which is based largely on the Stokes law radius of the ion in translational motion, is much less firm. Both ions have more NH protons than are required to form hydrogen bonds to all adjacent water molecules, and the resulting excess of hydrogen-bond donor sites is almost certain to promote molecular mobility in the hydration shell by permitting numerous hydrogen-bonded configurations of similar energy.

Experimental Part

Materials. Hexaamminoplatinum(IV) chloride was prepared by the procedure of Johnson, Basolo, and Pearson[11] from 28 g of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), 16 g of ammonium carbonate, and 100 ml of anhydrous ammonia. The mixture was allowed to stand in a high-pressure bomb at room temperature for 48 hr. After evaporation of the ammonia, the remaining solid was stirred with 60 ml of 1 *N* ammonium hydroxide (aqueous) and then with two 30-ml portions of 6 *N* HCl. The solid phase, which contained the desired hexaammino complex and lesser substitution products, was separated and treated with 230 ml of hot water, in which about half of it dissolved. On cooling of the hot solution and progressive evaporation of the solvent, seven fractions of crystalline solids were obtained. After vacuum drying at 100°, chloride analysis showed that the first three fractions consisted mostly of $Pt(NH_3)_6Cl_4$. Highly pure material was obtained by further recrystallization of these fractions from water–methanol. The samples used in the kinetic experiments analyzed for 32.0 and 32.2% ionic chloride (calcd for $Pt(NH_3)_6Cl_4$, 32.30%). The slight deficiency in chloride appeared to be due to the presence of some solid $(NH_3)_5PtNH_2Cl_3$, the conjugate base; potentiometric acid–base titration indicated the presence of 1.3% of a weak base. After a kinetic run, pure $Pt(NH_3)_6Cl_4$ was recovered by precipitation with methanol from the slightly acidified aqueous solution.

H_2O, D_2O, and water enriched in ^{17}O were redistilled in all-glass apparatus prior to use to remove any metal ions that might be present. Standard solutions for acidimetry and pH work were prepared as described previously.[9,12]

Electrolytic Properties. $_cK_a$ was measured potentiometrically, using a Beckman Research pH meter and a thermostated cell with glass electrode and saturated KCl|AgCl–Ag reference half-cell.[12] Conductivity measurements were made in collaboration with Mr. Charles D. Brown, using an a.c. bridge and detector provided by our physical chemistry laboratory. A known small amount of HCl was added to the $Pt(NH_3)_6Cl_4$ solutions in these measurements to repress acid dissociation. The cell constant of the water-jacketed conductivity cell was determined with a number of KCl solutions and was reproducible to ±0.05%. The absolute accuracy of the measurements is probably within 0.25%. In subtracting the conductivity of the added HCl, we used the known equivalent conductivity of HCl in water at the same ionic strength as that of the solutions. Results were [*formal concentration* × 10^3, *conductivity* (mho cm^{-1}) × 10^3, both of $Pt(NH_3)_6Cl_4$ in water at 25°]: 0.6245, 0.3772; 1.249, 0.7031; 2.498, 1.3095; 4.996, 2.392; 9.993, 4.382. We thank Mr. Charles D. Brown for his collaboration.

Nmr Measurement of Proton-Exchange Rates. τ_W and τ_{NH} were measured in H_2O, HOD–D_2O, and in ^{17}O-enriched solvents as described in previous publications from this laboratory.[9,16] Proton-exchange rates were calculated according to eq 6, 8, and 9 of ref 16, together with eq 18 of this paper, which is given below. Equation 18 relates the NH–OH exchange broadening, Δ_{NH}, to τ_{NH} and the NH-proton site fraction p. It takes into account the peculiar pattern of spin–spin interaction shown in Figure 1; 66.3% of the NH protons interact with ^{14}N and 33.7% interact with both ^{14}N and ^{195}Pt. Numerical values of nmr parameters used in this

$$\Delta_{NH} = \frac{0.663p}{3}\sum_i \frac{(\delta + iJ)^2\tau_{NH}}{1 + (\delta + iJ)^2\tau^2{}_{NH}} + \frac{0.337p}{6}\sum_i\sum_j \frac{(\delta + iJ + jJ')^2\tau_{NH}}{1 + (\delta + iJ + iJ')^2\tau^2{}_{NH}}$$
$$i = -1, 0, +1;\ j = -{}^1/_2, +{}^1/_2 \qquad (18)$$

calculation were as follows: $J_{NH} = J = 333$ sec^{-1} (53 Hz); $J_{PtH} = J' = 264$ sec^{-1} (42 Hz). δ is the NH–OH chemical shift difference; at our resonance frequency of 56.4 MHz, $\delta = 593$ sec^{-1} (1.673 ppm) in H_2O and 565 sec^{-1} (1.594 ppm) in HOD–D_2O (5 atom % H) at 25°. The experimental maxima in Δ_{NH} agreed with prediction based on these parameters within the experimental error

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(27) T. P. Pitner and R. B. Martin, *J. Amer. Chem. Soc.*, **93**, 4400 (1971).

(28) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **91**, 5227 (1969).

(29) W. R. Morgan and D. E. Leyden, *ibid.*, **92**, 4527 (1970). See also footnote 16 in ref 27.