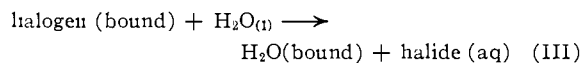


in explaining the invariance of the energy of activation from one halo complex to another. The reorientation of the solvent around the reacting complex must then be a real effect. The variable portion of this effect must be associated with the leaving group since it would appear to be the only variable within the system. If this is a correct assumption, then the differences in the entropy of activation between the complexes ought to roughly parallel the differences in the thermodynamic entropies of the reactions corresponding to I. Latimer and Jolly²⁵ have suggested a procedure for the estimation of the thermodynamic entropy of any reaction of this type. In general form this reaction is rewritten



Values that have been estimated²⁶ for the various entropy terms in III are 9.4 e.u. for bound water, 21 e.u. for free bromide, 16.7 for free water and 9 for bound bromide. These values lead to a calculated value for ΔS_1 for reaction 1 of +4.7 e.u. A similar treatment applied to the hydrolysis of the chloro and iodo complexes leads to values of +0.8 and 7.2 e.u., respectively. These values have

(25) W. M. Latimer and W. L. Jolly, *J. Am. Chem. Soc.*, **75**, 1548 (1953).

(26) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

approximately the same relationship to one another as do the entropies of activation for the hydrolysis reaction. The principal difference between the thermodynamic entropies of the reaction leading to the replacement of halogen by water in the complex is the entropy of formation of the various halide ions in solution (Cl^- , 15 e.u., Br^- , 21 e.u.; I^- 27 e.u.).²⁷ A correlation between the entropy of activation for the hydrolysis reaction and the thermodynamic entropy of hydration of the ion seems to be reasonable on the basis of this data. The relative order and magnitudes of these values is not greatly different from that observed between the entropies of activation for the three complexes. Such considerations as these indicate very strongly that the solvent sheath is a direct participant in both the $p\text{H}$ independent and the $p\text{H}$ dependent reactions. Furthermore the similarity of the variation of the entropy terms in the two reactions which behave so differently to changes in the $p\text{H}$ indicates that both have transition states which interact with the solvent sheath in the same way. There is however, no indication as to whether a single solvent molecule is specifically involved in the transition state. It is not possible then to assign these reactions on the basis of the observations reported in this paper to either of the S_N1 or S_N2 classifications.

(27) W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

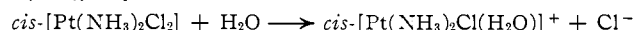
[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

cis-Dichlorodiammineplatinum(II). Acid Hydrolysis and Isotopic Exchange of the Chloride Ligands¹

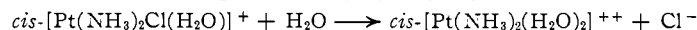
BY JOHN W. REISHUS AND DON S. MARTIN, JR.

RECEIVED OCTOBER 21, 1960

The acid hydrolysis of *cis*-[Pt(NH₃)₂Cl₂] has been studied at 25 and 35° For the first acid hydrolysis



the equilibrium constant, K_1 , is 3.3×10^{-3} mole/l. and the rate constant, k_1 , is 2.5×10^{-5} sec.⁻¹ at 25°. There is no significant direct exchange between the chloride ligands of *cis*-[Pt(NH₃)₂Cl₂] and Cl⁻. For the second acid hydrolysis



the equilibrium constant K_2 is 4×10^{-5} mole/l., at 25°. The exchange of chloride with *cis*-[Pt(NH₃)₂Cl(H₂O)] occurs at a rate which is chloride-independent and is characterized by a first order rate constant, $k_2 = 3.3 \times 10^{-5}$ sec.⁻¹ at 25°. It appears likely that this exchange also occurs by only an acid hydrolysis mechanism.

Introduction

When the compound which was originally designated by Werner^{2a} as *cis*-[Pt(NH₃)₂Cl₂] is dissolved in H₂O, the solution possesses the very low conductivity of a non-electrolyte. However, an increase in the conductivity of its solutions has been noted by a number of investigators.²⁻⁴ Jensen⁵ proposed that the increase in conductivity

(1) Contribution No. 924. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

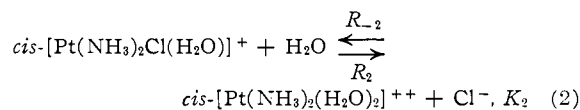
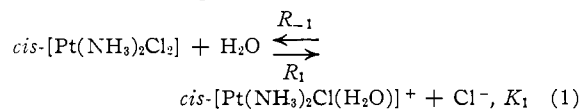
(2) (a) A. Werner, *Z. anorg. Chem.*, **3**, 267 (1893). (b) A. Werner and A. Miolati, *Z. physik. Chem.*, **12**, 49 (1893).

(3) H. D. K. Drew, F. W. Pinkard, W. Wardlaw and E. G. Cox, *J. Chem. Soc.*, 988 (1932).

(4) D. Banerjea, F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.*, **79**, 4055 (1957).

(5) K. A. Jensen, *Z. anorg. Chem.*, **229**, 252 (1936).

of the solutions upon aging can be explained in terms of acid hydrolysis or aquation of the chloride ligands according to



The R 's are the rates for the indicated reactions and the K 's are the equilibrium constants. In the present work, the rate expressions assumed to apply are

$$R_1 = k_1[\text{Pt}(\text{NH}_3)_2\text{Cl}_2] \quad (3)$$

$$R_{-1} = k_{-1}[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+][\text{Cl}^-] \quad (4)$$

$$R_2 = k_2[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+] \quad (5)$$

$$R_{-2} = k_{-2}[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2^{++}][\text{Cl}^-] \quad (6)$$

where the brackets imply concentrations of the enclosed species in mole/l.

Banerjea, Basolo and Pearson⁴ measured the rate at which Cl^- formed in solutions of *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ in 0.01 *M* NaNO_3 and concluded that at 25° k_1 was $3.8 \times 10^{-5} \text{ sec.}^{-1}$. They also noted that the rate of substitution was unchanged by the presence of 0.016 *M* NaOH .

The titration of the acidic hydrogen in the aquo-complexes of platinum(II) has served in this Laboratory to characterize the acid hydrolysis in the systems containing $[\text{PtCl}_4]^-$ and $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$.⁶⁻⁹

In the present investigation, this method has been applied to solutions of *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. Also, since the acid hydrolysis provides a means for the isotopic exchange of the chloride ligands with free chloride ion, this isotopic exchange has been measured to ascertain if alternative means for the exchange are important.

Experimental

Materials.—The *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ was synthesized from iridium-free $K_2[\text{PtCl}_4]$, whose preparation was described in an earlier work.⁹ The method of Lebedinskii and Golovnya¹⁰ was used in which 6 g. of KCl and 6 g. of $K_2[\text{PtCl}_4]$ were refluxed for 30 min. in a 20% ammonium acetate solution. After the solution cooled, the greenish-yellow precipitate was recovered. It was recrystallized three times from hot water which was acidified with HCl . Analyses of the product yielded: 64.7% Pt and 23.6% Cl. Calcd. 65.0% Pt and 23.6% Cl.

The ultraviolet absorption spectrum yielded the most sensitive criterion of purity. For a preparation a ratio of at least 4.5 for the absorbance of the peak at 300 $m\mu$ to the absorbance of the valley at 247 $m\mu$ was considered to represent a satisfactory purity (Cary Recording Spectrophotometer Model 12). When the compound was dissolved in H_2O , the molar conductivity initially observed was 1.7 l./mole ohm cm.

Chlorine-36 was obtained from the Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tennessee. The isotope was delivered in the form of approximately 2 *N* HCl , and it was used without further preparation.

The ion exchange resins used were Amberlite IR-120 for cations and Dowex 1 for anions, 50 to 100 mesh. The resins were packed in columns 2 cm. in diam. with 12-14 cm. beds. The beds were supported by coarse sintered glass filters to provide a rapid flow.

Other chemical reagents were of reagent grade materials which were certified to meet American Chemical Society specifications. All water was drawn from the distilled water tap and was then redistilled from alkaline permanganate.

Equipment and Methods.—The equipment and methods for the titrations of the hydrolysis products in the solution and for the preparation, counting and weighing of samples in the evaluation of specific activities of the radioactive samples have been described in the reported studies of $[\text{PtCl}_4]^-$ and $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$.⁶⁻⁹

Titrations of Equilibrium Solutions.—Equilibrium solutions of the desired concentration and volume were prepared

(6) L. F. Grantham, T. S. Elleman and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **77**, 2965 (1955).

(7) T. S. Elleman, J. W. Reishus and D. S. Martin, Jr., *ibid.*, **80**, 536 (1958).

(8) T. S. Elleman, J. W. Reishus and D. S. Martin, Jr., *ibid.*, **81**, 10 (1959).

(9) C. I. Sanders and D. S. Martin, Jr., *ibid.*, **83**, 807 (1961).

(10) V. V. Lebedinskii and V. A. Golovnya, *Izvest. Sektora Platiny i Drug. Blagorod. Metal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R.*, **20**, 95 (1947).

by dissolving the calculated quantity of *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and Na_2SO_4 , to yield an ionic strength of 0.318, in H_2O . Solutions were aged in a thermostat for one to three days to attain steady states. Generally, the solutions were kept in flasks that were covered with opaque tape to exclude light. Solutions were titrated with standard NaOH , and a glass indicator electrode was used. The end-points were taken from the maxima in plots of $\Delta\text{pH}/\Delta\text{ml}$. NaOH . An average pH of 8.9 was obtained for the end-points. After an end-point had been approximately established by a complete titration, additional samples were titrated rapidly by adding a sufficient amount of base initially to approach the end-point. Titres of equilibrium solutions are given in Table I.

Determination of the Rate of the First Acid Hydrolysis.

Freshly prepared solutions of *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and Na_2SO_4 were placed in a thermostat. Aliquots were withdrawn at intervals and were titrated to evaluate the extent of hydrolysis as a function of time. Typical results for two solutions have been plotted in Fig. 1. The rates of the acid hydrolysis were obtained from the initial slopes of such curves. There was some ambiguity in locating the origin for these plots because 10 to 30 minutes were required to dissolve the solid compound completely. The time of dissolving was dependent somewhat upon the concentration to be attained and varied between different preparations. The initial portions of the curves were approximately linear and gave a well defined slope which could be used for a satisfactory evaluation of an initial reaction rate.

Isotopic Exchange of Chloride.—Initially, the obvious procedure for the separation of free chloride ion from the complexed chloride by precipitation as AgCl was attempted. However, a separation-induced exchange occurred in such cases which precluded consistent results for the exchange kinetics and the method was abandoned.

The ion exchange separation, which proved satisfactory, was developed next. The exchange was initiated by the addition from a micropipet of a quantity of the tracer Cl^- solution (5-20 μ l.) so that only a negligible change in volume of Cl^- concentration resulted. At intervals thereafter aliquots (15-25 ml.) were withdrawn from the solutions and passed through an anion exchange column in the nitrate form. The column was washed with 100 ml. of water. This operation required 12-20 min. The anion exchanger effectively removed free chloride ion, and the effluent was assumed to contain the *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})]^+$ without fractionation.

Other aliquots from the exchange solutions were passed through both the anion exchange column and a cation exchange column in the sodium form. These columns also were washed with 100 ml. of H_2O , to leave only *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ in the effluent. Solutions collected from the ion exchange columns were heated for 30 min. with excess aqueous NH_3 to displace the complexed chloride. Finally, the solutions were acidified, and AgNO_3 was added to precipitate AgCl . The specific activity of the AgCl (cts./min. mg. Cl) was determined.

Exchange solutions were prepared by weighing the calculated amounts of *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, KCl and Na_2SO_4 into a volumetric flask and adding H_2O to the mark. For the evaluation of exchange rates in equilibrium systems the solutions were aged for 1-3 days in a thermostat before the chloride tracer was added. The solutions were generally contained in flasks covered with opaque tape, but in a few cases the solutions were exposed to laboratory lights without any observed effect. In several experiments exchange was initiated immediately after the solution was prepared. Such experiments make possible the evaluation of direct exchange between Cl^- and *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ which may occur before the formation of significant quantities of the hydrolysis products. Results with typical aged solutions are in Fig. 2, and some fresh-solution exchanges are shown in Fig. 3.

Treatment of Data.—For the treatment of the kinetics and exchange the following terms are defined:

- a = total concentration of Pt in the solu. (added as *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, mole/l.
- b = initial concentration of Cl^- , added as KCl
- s = concn. of Cl^{36} in Cl^- , cts./min. l.
- u = concn. of Cl^{36} in *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, cts./min. l.
- v = concn. of Cl^{36} in *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})]^+$, cts./min. l.

$I = u + v + s = \text{concn. total Cl}^{36}$

$S = s/[\text{Cl}^-]$. (Specific activity of chloride ion)

$U = u/2[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. (Specific activity of *cis*-[Pt-(NH₃)₂Cl₂])

$V = v/[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+]$. (Specific activity of *cis*-[Pt(NH₃)₂Cl(H₂O)]⁺)

$T = \text{titer of solution, equivalents of acid/l.}$

Equilibrium quantities are indicated by a ∞ subscript and initial quantities by a 0 subscript.

Aquation Reactions.—If one proton from each complexed H₂O is titrated, the titer for the solution is

$$T = [\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+] + 2[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2^{++}] \quad (7)$$

It was shown in earlier work⁹ that the titer in the equilibrium system satisfies the expression

$$K_1(b + T_\infty)(a - T_\infty) + K_1K_2(2a - T_\infty) = T_\infty(b + T_\infty)^2 \quad (8)$$

K_1 and K_2 are equilibrium concentration quotients for reactions 1 and 2 which were presumed to be constants since the ionic strength was maintained nearly constant at 0.318 mole/l. in all the experiments.

If the titers of a freshly prepared solution of *cis*-[Pt-(NH₃)₂Cl₂] were measured at intervals after its preparation, the rate constant for reaction 1, k_1 , was obtainable from the expression

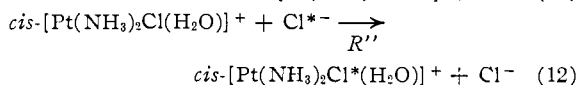
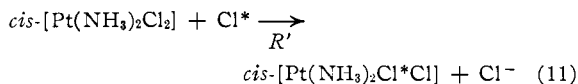
$$k_1 = (dT/dt)_0/a \quad (9)$$

The rate constant k_{-1} was then obtained from the familiar expression

$$k_{-1} = k_1/K_1 \quad (10)$$

No unambiguous method was found for the evaluation of k_2 and k_{-2} .

Exchange in Aged Solutions.—Reactions 1 and 2 provide for the introduction of tagged (Cl³⁶)⁻ into the complexes. However, alternative direct exchange processes may occur which will be written



The differential equations for the rate of appearance of radioactive chlorine in the complexes are then

$$du/dt = -R_1 2U + R_{-1}(V + S) + R'(S - U) \quad (13)$$

and

$$dv/dt = R_1 U - R_{-1} V - R_2 V + R_{-2} S + R''(S - V) \quad (14)$$

Under the conditions of equilibrium with respect to reactions 1 and 2 (aged solution exchange), $R_1 = R_{-1}$, $R_2 = R_{-2}$, and R' and R'' can be considered constants. Equations 13 and 14 become first order linear differential equations for u and v , and they possess solutions with a double exponential form

$$1 - u/u_\infty = A_1 e^{-\alpha_1 t} + A_2 e^{-\alpha_2 t} = 1 - U/U_\infty \quad (15)$$

$$1 - v/v_\infty = B_1 e^{-\alpha_1 t} + B_2 e^{-\alpha_2 t} = 1 - V/V_\infty \quad (16)$$

Although these solutions are double exponentials, exchange variables such as U/U_∞ and V/V_∞ can be followed with reasonable accuracy only from the starting values of 0 to about 0.7–0.8. In this region the semi-log plots of $(1 - U/U_\infty)$ and $(1 - V/V_\infty)$ deviate only slightly from straight lines and the curves can not be resolved into the two components. However, the time for half-exchange of a fraction serves as a useful parameter. For the fraction *cis*-[Pt-(NH₃)₂Cl₂] the time of half-exchange is defined as the time, $T_{1/2u}$, at which $(U - U_0)/U_\infty - U_0/U_\infty = 1/2$ and similar expressions serve for the V and S variables. It is to be emphasized that in a three component system such as this, the time of half-exchange is different for the various fractions, and the time for $3/4$ exchange for a fraction does not equal $2 \times T_{1/2}$ for that fraction. Also, values for a fraction of exchange > 1 are obtainable under certain conditions.

It was found that the rate of exchange of the *cis*-[Pt-(NH₃)₂Cl₂] fraction was relatively insensitive to the rates R_2 or R'' . It was not possible to isolate the [Pt(NH₃)₂-

Cl(H₂O)]⁺ fraction but the anion exchange separation procedure was devised to leave the [Pt(NH₃)₂Cl₂] and [Pt(NH₃)₂Cl(H₂O)]⁺ in solution so that $(u + v)$ could be measured. From eq. 15 and 16 it is clear that

$$\left(1 - \frac{u + v}{u_\infty + v_\infty}\right) = C_1 e^{-\alpha_1 t} + C_2 e^{-\alpha_2 t} = 1 - F_{u+v} \quad (17)$$

The quantities, α_1 , A_1 , B_1 , C_1 , in the solutions of the exchange, eq. 15, 16 and 17, can be evaluated from the quantities a , b , K_1 , K_2 , k_1 and the natural parameters $R'/R_{\pm 1}$, $R_2/R_{\pm 1}$ and $R''/R_{\pm 1}$. Since it was not possible to separate the reaction rates, $R_{\pm 2}$ and R'' , a single parameter $(R_{\pm 2} + R'')/R_{\pm 1}$ was used in place of the last two. From a set of calculated values of the α_1 , A_1 , and C_1 the times of half-exchange, $T_{1/2u}$ and $T_{1/2(u+v)}$, were readily obtained from plots of the corresponding calculated fractions of exchange.

Exchange in Fresh Solutions.—The rate of exchange in freshly prepared solutions of *cis*-[Pt(NH₃)₂Cl₂] gives additional information about the magnitude of R' . Under the condition that $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+] \ll a < b$ the approximation for Eq. 13 can be written

$$du/dt = k_{-1}[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+] I + k' a b^{n-1} I \quad (18)$$

where R' is taken as first order in [Pt(NH₃)₂Cl₂] and n th order in Cl⁻. During the interval that eq. 18 is valid, the concentration of [Pt(NH₃)₂Cl(H₂O)]⁺ is given by

$$[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+] = [\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+]_0 + k_1 a t \quad (19)$$

A concentration, [Pt(NH₃)₂Cl(H₂O)]₀, greater than zero is required because 15–20 min. are needed to dissolve the samples before the exchange can be started. The integration of eq. 18 under these conditions yields

$$U/U_\infty = \{k_{-1}[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+]_0 (b + 2a)t/2a\} + \{k_{-1}k_1(b + 2a)t^2/4\} + \{k'b^{n-1}(b + 2a)t/2\} \quad (20)$$

This equation is a very satisfactory approximation for values of U/U_∞ of less than 0.2.

Results and Discussion

The titers of equilibrium solutions at 25 and 35° have been listed in Table I. In several cases the experiments were repeated, and the reproducibility was generally within $\pm 3\%$. Because of the low

TABLE I

TITRATION OF AGED SOLUTIONS OF *cis*-[Pt(NH₃)₂Cl₂]-EQUILIBRIUM CONSTANTS FOR ACID HYDROLYSIS

Initial [Pt-(NH ₃) ₂ Cl ₂] ^a	Initial [KCl] ^b	Calcd. [Pt-(NH ₃) ₂ Cl-(H ₂ O)] ⁺	Calcd. [Pt-(NH ₃) ₂ Cl-(H ₂ O)] ⁺	Titer, Obsd.	"T" _{1/2} , Calcd.
25.0°					
K_1 (average) = 3.3×10^{-3} mole/l.		K_2 (average) = 4×10^{-4} mole/l.			
2.50	0	1.36	0.31	1.97	1.98
2.50	1.00	1.27	.21	1.68	1.68
5.00	0	2.40	.34	3.08	3.10
5.00	1.03	2.21	.26	2.72	2.73
35°					
K_1 (average) = 3.9×10^{-3} mole/l.		K_2 (average) = 2×10^{-4} mole/l.			
1.50	0	1.01	0.16	1.32	1.31
2.50	0	1.57	.16	1.90	1.90
5.00	0	2.71	.18	3.06	3.06

^a All concentrations are $10^3 \times$ mole/l.

solubility of the compound and the need for sufficient concentrations to provide satisfactory titrations, the extent of the concentration range was not high. Equilibrium constants, K_1 and K_2 , were calculated by the use of Eq. 8 from each combination of two titrations at a given temperature. The

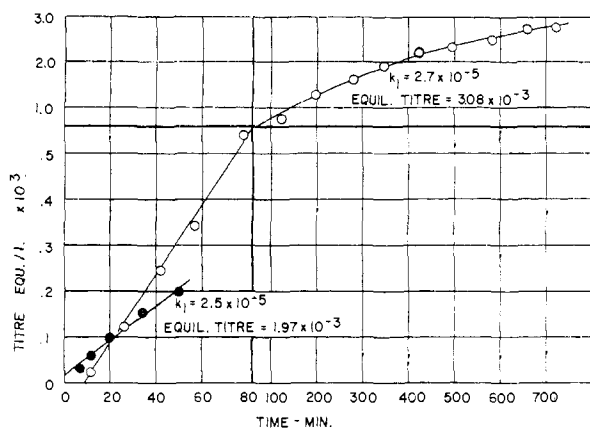


Fig. 1.—Titer of *cis*-[Pt(NH₃)₂Cl₂] solutions vs. time, temp. = 25°, μ = 0.318. ●, initial concentration = 0.0025 mole/l., ○, initial concn. = 0.0050 mole/l.

averages of these calculated constants are in Table I. The concentration of each of the complex species and the titer, calculated from the equilibrium constants, have been included for each experiment in Table I. The agreement of these calculated titers with the observed values attests to the consistency of the equilibrium constants. It is noted that the calculated concentration of the [Pt(NH₃)₂(H₂O)₂]⁺⁺ was never large and, therefore, the constant K_2 was not well defined. If for the 25° experiments, K_2 was arbitrarily set equal to zero and K_1 was calculated from the experiment at $a = 5.00 \times 10^{-3}$ mole/l. and $b = 0$, the calculated titer for $a = 2.50 \times 10^{-3}$ mole/l. and $b = 0$ was 8% low. This deviation in the calculated titer was well outside the experimental reproducibility, and the result indicated that the second aquation was real. It was calculated, however, that a 3% change in one titer of these two experiments changed pK_1 by 0.10 and pK_2 by 0.25. This result also indicates the greater uncertainty in K_2 . Some of the equilibrium solutions were prepared with added KCl to assure that a possible small chloride impurity did not seriously affect the data.

The value of K_1 for *cis*-[Pt(NH₃)₂Cl₂] is about one order of magnitude smaller than the constants for [PtCl₄]⁻ and [Pt(NH₃)Cl₃]⁻, which are nearly equal. However, K_2 for *cis*-[Pt(NH₃)₂Cl₂] is, approximately equal to the value for [PtCl₄]⁻, which in turn about an order of magnitude larger than the constant for [Pt(NH₃)Cl₃]⁻. Although the data are not sufficiently precise to permit a good evaluation of ΔH^0 for the reactions, they are at most only a few kcal. in all cases. The effect of the structure on the relative stability of the hydrolysis species in aqueous solutions is apparently subtle with no outstanding trends.

The rate constants for the first acid hydrolysis, k_1 , were obtained from the graphs, of which those in Fig. 1 are typical, by the application of eq. 9.

In five determinations at 25° in which the initial *cis*-[Pt(NH₃)₂Cl₂] concentration ranged from 2.5–6.0 $\times 10^{-3}$ mole/l., values for k_1 of 2.5–2.7 $\times 10^{-5}$, av. 2.5×10^{-5} sec.⁻¹, were obtained. In four experiments at 35° with the initial *cis*-[Pt(NH₃)₂Cl₂] concentrations in the range of 2.5–5.0 $\times 10^{-3}$ moles/l., the values for k_1 of 7.2–8.1 \times

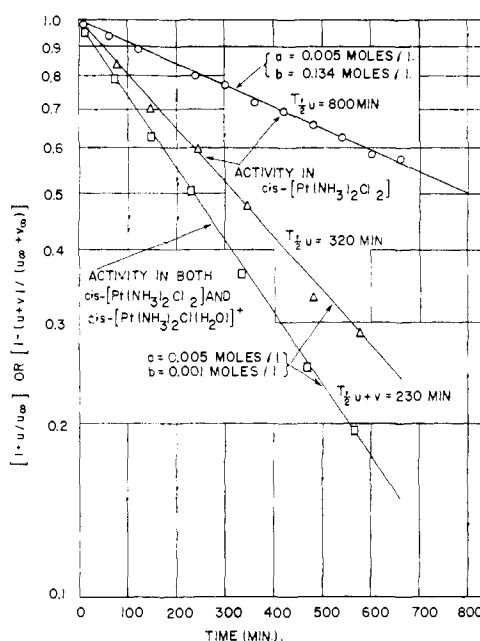


Fig. 2.—Typical exchange experiments in aged (equilibrium) solutions of *cis*-[Pt(NH₃)₂Cl₂]. Temp. = 25°, μ = 0.318.

10^{-5} , av. 7.6×10^{-5} sec.⁻¹, were obtained. All of these results were for solutions in which an ionic strength of 0.318 mole/l. was established by the addition of Na₂SO₄. They indicated a $\Delta H_1^\ddagger = 19.7$ kcal., and $\Delta S^\ddagger = -14$ e.u. for reaction 1.

The value at 25° of 2.5×10^{-5} sec.⁻¹ for k_1 is in rather poor agreement with the value of 3.8×10^{-5} sec.⁻¹ reported by Banerjee, *et al.*⁴ They measured the appearance of Cl⁻ and presumably prepared the semi-log plot, $\log(1 - [\text{Cl}^-]/[\text{Cl}^-]_\infty)$ vs. time, which is normally prepared for a first order non-reversible reaction. Plots of $\log(1 - T/T_\infty)$ vs. time have been prepared from the data of the present experiments. These plots exhibited a definite although not large curvature. It was noted that $\ln 2$ divided by the time at which $T/T_\infty = 1/2$ agreed fairly well with the value reported by Banerjee, *et al.* It is believed, therefore, that their high value resulted from a failure to consider the reversibility of Reaction 1 or the possibility of the second aquation.

The results of some typical exchange experiments are shown in Figs. 2 and 3. The effectiveness of the ion exchange procedure in removing the ionic components is clearly shown in Fig. 3 from which it can be seen that any apparent exchange, induced by the separation procedure or resulting from its failure to achieve complete separation of Cl⁻, was of the order of 0.5 to 1.0%. The conditions for all of the exchange experiments with aged solutions together with the observed times of half-reaction have been included in Table II. For equilibrium solutions which contained high Cl⁻ concentration (>0.1 M), the concn. of [Pt(NH₃)₂Cl(H₂O)]⁺ was very low. In practice, only the specific activity of *cis*-[Pt(NH₃)₂Cl₂] in these systems could be determined. The half-time exchange for these chloride solutions were calculated with the assumption that $R' = 0$ and that $(R_2 + R'') \ll R_1$ (eq

TABLE II
EXCHANGE BETWEEN CHLORIDE, $cis\text{-[Pt(NH}_3)_2\text{Cl}_2]$ AND $cis\text{-[Pt(NH}_3)_2\text{Cl(H}_2\text{O)}]^+$ IN EQUILIBRIUM SOLUTIONS. IONIC STRENGTH = 0.318

Initial $[\text{Pt(NH}_3)_2\text{Cl}_2]$ $\cdot a$ moles/l. $\times 10^3$	Initial $[\text{KCl}]$ $\cdot b$ mole/l. $\times 10^3$	Equilibrium $[\text{Pt(NH}_3)_2\text{Cl(H}_2\text{O)}]^+$ ∞ mole/l. $\times 10^3$	Equilibrium $[\text{Pt(NH}_3)_2\text{(H}_2\text{O)}_2^{++}]$ ∞ mole/l. $\times 10^3$	Times of half-exchange				$(R_2 + R'')/R_1$
				Obsd., hr.	Calcd., hr.	Obsd., hr.	Calcd., hr.	
25°								
5.00	1.00	2.22	0.26	5.32	5.00	3.90	3.80	1.0
5.00	2.50	1.96	.18	5.50	5.50	4.33	4.30	0.9
5.00	5.00	1.60	.10	6.40	6.20	..	5.20	.7
5.00	10.00	1.13	.04	7.45	7.40	6.90	6.80	.5
5.00	134	0.12	..	13.3	14.5	..	14.5	..
5.0	268	.06	..	13.8	14.9	..	14.9	..
2.5	134	.06	..	13.8	15.0	..	15.0	..
35°								
5.0	2.50	2.19	0.09	2.32	2.00	1.48	1.53	1.0
5.0	10.0	1.28	0.02	2.75	2.54	2.36	2.32	0.6
5.0	134	0.14	..	4.33	5.04	..	5.04	..

15. These calculated values are included in Table II under the column $\tau_{1/2}$ -calcd.. The satisfactory agreement between these calculated and observed times of half-exchange indicate that the first acid hydrolysis, Reaction 1, accounts for the exchange between $cis\text{-[Pt(NH}_3)_2\text{Cl}_2]$ and Cl^- and that any contribution of Reaction 11, which is first or higher order in chloride, is negligible.

The chloride exchange for fresh solutions were investigated to explore the possibility of a contribution of Reaction 11 which might be zero order in chloride. In Fig. 3 are plotted values of U/U_∞ for a freshly prepared and for an aged solution of $cis\text{-[Pt(NH}_3)_2\text{Cl}_2]$. The uncertainty of 0.5-1.0%, introduced by the separation procedure, limit the conclusions concerning the initial exchange rate. However, it can be seen that in the aged solutions the introduction of the tracer into $cis\text{-[Pt(NH}_3)_2\text{Cl}_2]$ satisfactorily follows the calculated curve. Further, the introduction of tracer into $cis\text{-[Pt(NH}_3)_2\text{Cl}_2]$ in the fresh solution occurred at a much lower rate than in the equilibrium solution, and the experimental points in Fig. 3 rather satisfactorily followed the curve which was calculated with the assumptions that $R' = 0$ and that the time for dissolving the solid compound was equivalent to 10 min. It has been concluded, therefore, that any direct exchange for Reaction 11 which is zeroth order in chloride also must be less than 10% of the acid hydrolysis. It is noted that the isotopic exchange process is considerably slower than would be possible with the higher hydrolysis rate constant of Banerjea, *et al.*⁴

For exchange experiments in which the chloride concentration was low so that appreciable concentrations of $[\text{Pt(NH}_3)_2\text{Cl(H}_2\text{O)}]^+$ existed, the observed times of half exchange, $\tau_{1/2u}$ and also $\tau_{1/2(u+v)}$, when the latter was determined, have been included in Table II. In the analysis of this data, it was assumed that there was no fractionation of $[\text{Pt(NH}_3)_2\text{Cl}_2]$ and $[\text{Pt(NH}_3)_2\text{Cl(H}_2\text{O)}]^+$ in the anion exchange columns. In general, weights of AgCl counting samples corresponded rather closely to the expected weights of total chloride so that it is believed that fractionation was not serious. Since $\tau_{1/2(u+v)}$ was generally smaller than $\tau_{1/2u}$, a sub-

stantial rate for either Reaction 2 or Reaction 12 was indicated. The times of half-exchange were calculated for various values of the parameter, $(R_2 + R'')/R_1$, and under the condition that $R' = 0$. The value of this parameter, to the nearest 0.1, which was considered to give the most satisfactory set of times of half-exchange have been

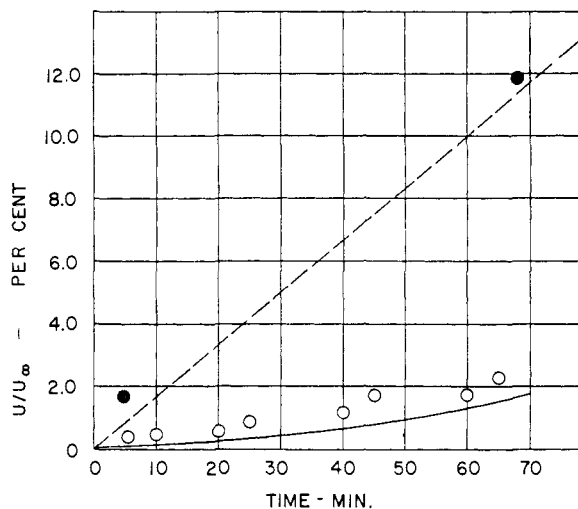


Fig. 3.—Initial part of exchange experiments for aged and fresh solutions of $cis\text{-[Pt(NH}_3)_2\text{Cl}_2]$. Temp. = 25°, $\mu = 0.318$, $a = 5.0 \times 10^{-3}$ mole/l. and $b = 5.0 \times 10^{-3}$ mole/l. O, exchange in fresh solution; ●, aged solution — $[\text{Pt(NH}_3)_2\text{Cl(H}_2\text{O)}]^+ = 1.60 \times 10^{-3}$ mole/l., $[\text{Pt(NH}_3)_2\text{(H}_2\text{O)}_2^{++}] = 0.10 \times 10^{-3}$ mole/l.; —, calculated curve, fresh solution: $U/U_\infty = \{k_{-1}[\text{Pt(NH}_3)_2\text{Cl(H}_2\text{O)}]_0 (b + 2a)t/2a\} + \{k_{-1}k_1t^2(b + 2a)/4\}$ where $[\text{Pt(NH}_3)_2\text{Cl(H}_2\text{O)}]^+_0 = 9 \times 10^{-5}$ mole/l. (10 minutes aging); — — —, calculated curve aged solution: $U/U_\infty = k_1(b + 2a)t/2[\text{Cl}^-]$.

indicated in Table II. Also included are the calculated values for these times of half-exchange. It can be seen that it has been possible to select values of $(R_2 + R'')/R_1$ which account rather well for the observed times of half-exchange. However, since it is the exchange of all the ligand-chloride which was measured, the relative uncertainty in the parameter becomes rather large, especially for

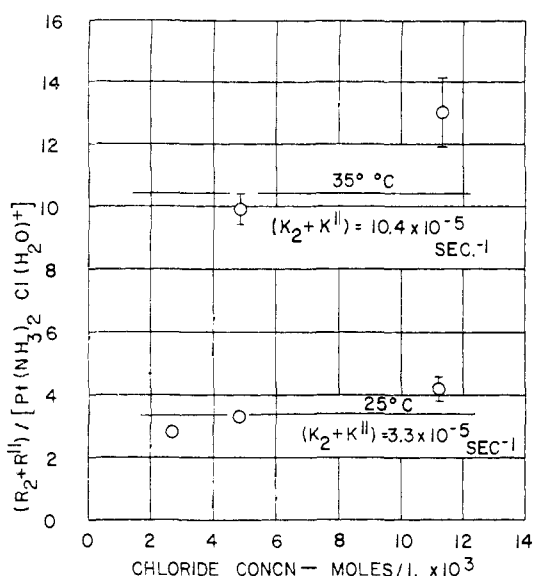


Fig. 4.—Plots of $(R_2 + R'')/[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+]$ vs. chloride concentration. Indicated $\Delta H^* = 20.3$ kcal., $\Delta S^* = -11$ e. u.

values of the parameter less than 1.0. In Fig. 4 has been plotted the quantity $(R_2 + R'')/[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+]$ vs. $[\text{Cl}^-]$ for all cases in which it was calculated. Although the values do increase somewhat with $[\text{Cl}^-]$, it was felt that the increase was not significant in view of the uncertainty in the parameter at the higher chloride concentration. It has been concluded, therefore, that the reaction rate sum $(R_2 + R'')$ is substantially zero order in chloride. The weighted averages for the indicated first order rate constants $(k_2 + k'')$, together with

values for ΔH^\ddagger and ΔS^\ddagger have been included with the data in Fig. 4.

It has not been possible to separate the individual reaction rates R_2 and R'' . Since reaction 12, with the rate R'' , is chloride independent and is not a solvation process, it presumably would have to proceed by a dissociative mechanism. It is possible that the entire exchange is carried by the acid hydrolysis, *i.e.*, $k'' \ll k_2$.

In the experiments which have been completed with the systems of $[\text{PtCl}_4]^-$, $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$ and *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]^-$, it has been found that the acid hydrolysis accounts completely for the exchange of the species, $[\text{PtCl}_4]^-$ and *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]^-$. All the other exchange processes in these systems are also chloride independent. In addition, all these first order reaction rate constants lie in the narrow range of $2.5-10 \times 10^{-5}$ sec.⁻¹, and all indicate rather similar entropies and energies of activation.

Basolo and Pearson¹¹ have indicated that the similarity of reaction rates for complex species whose charges ranged from -2 to 1 indicate that a simple dissociative mechanism to a coordination of 3 does not occur in the substitution reaction. The present experiments appear to support such a conclusion. It does appear likely that all the chloride exchange processes in these three systems occurs by the acid hydrolysis, and the chloride ion cannot compete with the solvent in the replacement of a chloride ion under the concentration conditions which have been studied. Apparently, the water ligand can be replaced rapidly by chloride or by many other substituting groups so the rate of the acid hydrolysis controls the rate of many substitution reactions, including the rate of base hydrolysis.

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Lower Oxidation States of the Lanthanides. Neodymium(II) Chloride and Iodide¹

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Investigation of the salt-rich portions of the Nd-NdCl₃ and Nd-NdI₃ phase diagrams establishes the existence of the incongruently melting NdCl_{2.3} (680°), NdCl_{2.2} (702°) and NdCl_{2.00} (841°) and the congruently melting NdI_{1.96} (562°). Neodymium(II) chloride is isomorphous with SmCl₂ and NdI_{1.96} with SmBr₂. The composition and powder patterns of solid solutions of cerium in NdCl_{2.3}, suggest substitution of a reduced cerium species, presumably Ce⁺², therein. The formation of a face-centered-cubic (Nd, Ce)Cl_{2.20} phase at higher Nd/Ce ratios is considered in terms of anion substitution in the body center of the fluorite structure. A new method is given for the preparation of the pure rare earth metal trichlorides and iodides by the reaction of HCl or I₂ with the metals in molybdenum or tungsten containers, respectively.

Introduction

The solubilities of certain metals in their molten salts have evoked considerable interest in recent years as the chemist has turned to the study of reactions at higher temperatures. Recent investigations have centered upon the alkali²⁻⁴

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