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Chlorotriammineplatinum(II) Ion. Acid Hydrolysis and Isotopic Exchange of Chloride Ligand[1,2]

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The acid hydrolysis of $[Pt(NH_3)_3Cl]^+$ has been shown to occur to a measurable extent. For this reaction: $[Pt(NH_3)_3Cl]^+ + H_2O \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} [Pt(NH_3)_3(H_2O)]^{+2} + Cl^-$, the equilibrium quotient was measured at 25 and 35°. At 25° the quotient was 8.4×10^{-5} at μ (ionic strength) = 0 and 27×10^{-5} at $\mu = 0.318$ *M*. This variation is consistent with the expected changes in activity coefficients. $\Delta H^0 \approx 0$. $k_1 = 2.6 \times 10^{-5}$ sec.$^{-1}$ at 25°, and it is nearly independent of μ. The acid hydrolysis provides a mechanism for the exchange of the chloride ligand and Cl^-. Exchange experiments with Cl^{36} showed that in addition to the acid hydrolysis, a process, first order in both $[Pt(NH_3)_3Cl]^+$ and Cl^-, with a rate constant of 7×10^{-5} M^{-1} sec.$^{-1}$, contributes to the exchange. The behavior of the entire series of chloroammines of platinum(II) toward acid hydrolysis and chloride exchange has been summarized, and a likely mechanism for the processes has been discussed.

Introduction

The potentiometric titration of a proton in the water–ligand system has served to characterize the kinetics and the equilibria for the acid hydrolysis of $[PtCl_4]^{-2}$, $[Pt(NH_3)Cl_3]^-$, and *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ in aqueous solutions.[4a–f]

For each of the previous complexes with the exception of *trans*-$[Pt(NH_3)_2Cl_2]$ the isotopic exchange of chloride ligands with chloride ion has been shown to occur only by acid hydrolysis (aquation) or by processes independent of chloride ion which possibly could be acid hydrolysis. With *trans*-$[Pt(NH_3)_2Cl_2]$ an exchange process proportional to the product of the complex concentration and the chloride ion concentration has been observed in addition to the acid hydrolysis. The present work includes an investigation of the ion $[Pt(NH_3)_3Cl]^+$ by these techniques and completes studies for the entire series of the chloroammineplatinum(II) complexes.

Banerjea, Basolo, and Pearson[5] reported that the acid hydrolysis equilibrium constant was immeasurably small in experiments designed to measure the increase of chloride ion concentration. From the isotopic exchange of chloride ion with the ligand, they obtained a first order rate constant of 1.5×10^{-5} sec.$^{-1}$ at 25°. Since this process was independent of chloride ion, it presumably characterized the acid hydrolysis. However, the present work has indicated that the equilibrium constant and the rate constant can be measured experimentally by the acid titration technique. Grinberg, *et al.*,[6] have reported that the rate of substitution of chloride by hydroxide is independent of hydroxide concentration, and at 25° they reported a first order rate constant of 2.2×10^{-5} sec.$^{-1}$. Accordingly, they proposed that the hydroxide substitution occurred *via* an acid hydrolysis step.

Experimental

Chlorotriammineplatinum(II) sulfate was prepared by the method of Chatt, Gamlen, and Orgel.[7] The salt was crystallized twice from dilute KCl solutions and was recrystallized several times from water until no changes in the ultraviolet spectrum of the product occurred. Platinum in the preparations was determined gravimetrically following thermal decomposition at 650°. For chloride, solutions were boiled for a few minutes with excess ammonia. After acidification of the solution, $AgNO_3$ was added to precipitate the chloride, which was determined gravimetrically. Analyses for a typical preparation:

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[4] (a) L. F. Grantham, T. S. Elleman, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **77**, 2965 (1955); (b) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *ibid.*, **80**, 536 (1958); (c) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *ibid.*, **81**, 10 (1959); (d) C. I. Sanders and D. S. Martin, Jr., *ibid.*, **83**, 807 (1961); (e) J. W. Reishus and D. S. Martin, Jr., *ibid.*, **83**, 2457 (1961); (f) D. S. Martin, Jr., and R. J. Adams, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 579–589.

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

[6] A. A. Grinberg, S. S. Borsakova, I. N. Kukuskin, V. E. Mironov, L. E. Nikol'skaja, D. B. Smolenskja, and G. A. Sagisultanova, *Svensk Kem. Tidskr.*, **73**, 199 (1961).

[7] J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

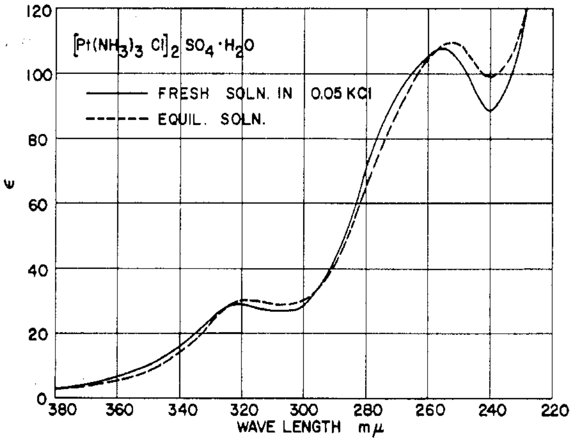

Fig. 1.—Ultraviolet absorption spectra for 1.5 m*M* solution of $[Pt(NH_3)_3Cl]_2SO_4{\cdot}H_2O$ at 25°. Extinction coefficient, based on one formula weight of the $[Pt(NH_3)_3Cl]^+$ ion, *vs.* wave length. Cary Model 12 recording spectrophotometer.

Calculated for $[Pt(NH_3)_3Cl]_2SO_4{\cdot}H_2O$: Pt, 57.62; Cl, 10.46. Found: Pt, 57.5; Cl, 10.6.

Since the ultraviolet absorption spectrum appears to give the best criterion for purity, the spectrum of our product is presented in Fig. 1. This spectrum is similar to but not identical with the spectrum of Chatt, *et al.*[7] The extinction coefficient is somewhat lower over the spectrum than they reported. The low valley at 240 mμ of the present spectrum probably signifies a somewhat purer sample. In six preparations the extinction coefficient for the peak at 255 mμ differed by less than 1.5%. The spectrum in Fig. 1 was obtained with chloride to suppress the acid hydrolysis. A spectrum of a solution in which the acid hydrolysis equilibrium was established is shown also. The solution of Chatt, *et al.*,[7] may have contained appreciable quantities of $[Pt(NH_3)_3(H_2O)]^{+2}$.

Procedures and equipment for the titrations have been described in earlier publications.[4a-f] Isotopic exchange experiments involved only solutions which were at equilibrium with respect to the acid hydrolysis reaction. The exchange was initiated by the addition of a few microliters of HCl solution, tagged with Cl^{36}. At subsequent intervals aliquots of the solution were removed and passed through an anion exchange resin to remove chloride ion, following the techniques used for the *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$. The chloride ligand from the complexes in the effluent was removed by heating with ammonia and the chloride in solution then was precipitated as silver chloride. The procedures and precautions for preparing, weighing, and counting the samples have followed those in the earlier work.

Results and Discussion

Acid Hydrolysis Equilibrium.—With $[Pt(NH_3)_3Cl]^+$ only a single acid hydrolysis of chloride is possible, according to eq. 1.

$$[Pt(NH_3)_3Cl]^+ + H_2O \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} [Pt(NH_3)_3(H_2O)]^{+2} + Cl^- \qquad (1)$$

Equilibrium solutions were prepared by first dissolving the compound $[Pt(NH_3)_3Cl]_2SO_4{\cdot}H_2O$ and an additional salt to establish the desired ionic strength in water. The solutions then were allowed to stand in a thermostat for at least 24 hr. The initial concentrations and the resulting titers for the equilibrium solutions, T_∞, are included in Table I. The equilibrium constant for the acid hydrolysis is given by

$$K = \frac{[Pt(NH_3)_3(H_2O)^{+2}][Cl^-]\gamma_2\gamma_{Cl}}{[Pt(NH_3)_3Cl^+]\gamma_1} = \frac{T_\infty(b + T_\infty)\gamma_2\gamma_{Cl}}{(a - T_\infty)\gamma_1} \qquad (2)$$

where:

a = the initial concentration of $[Pt(NH_3)_3Cl]^+$ (M) (before aging)
b = initial concentration of Cl^- (M) (before aging)
γ_2 = activity coefficient of $[Pt(NH_3)_3(H_2O)]^{+2}$
γ_{Cl} = activity coefficient of Cl^-
γ_1 = activity coefficient of $[Pt(NH_3)_3Cl]^+$

For solutions in which the ionic strength was established by the addition of relatively large amounts of Na_2SO_4 or $NaClO_4$, the concentration quotient, K', defined by eq. 3, was considered to be constant. The quotient for each of the solutions has been included in Table I. For solutions

$$K' = K\gamma_1/\gamma_{2Cl} \approx K/\gamma_2 \qquad (3)$$

with no added salt γ_2 was set equal to $(f_{C_2O_4^{-2}}/f_{HC_2O_4^-}f_{Cl^-})\gamma_\pm^2$. The quantity $(f_{C_2O_4^{-2}}/f_{HC_2O_4^-}f_{Cl^-})$ was evaluated for a range of ionic strengths by Pinching and Bates[8] in the potentiometric determination of the ionization constants of oxalic acid, and $\gamma_\pm^2$ was obtained from the activity coefficient of HCl in a solution of KCl of the corresponding ionic strength.[9]

The equilibrium constant for the acid hydrolysis is comparable in magnitude to that for *trans*-$[Pt(NH_3)_2Cl_2]$. Accordingly, the acid hydrolysis is only important in rather dilute solutions which are free of added chloride ion. The dependence upon ionic strength, which is opposite in sign to that for $[PtCl_4]^{-2}$, is consistent with the expected variation in the activity coefficient, γ_2. Since in solutions of 1 to 4 m*M* the extent of the acid hydrolysis amounts to 15 to 30%, the equilibrium constant is given rather precisely by the experiments. The indicated negligible temperature dependence of K indicates that ΔH^0 is small.

Kinetics for Acid Hydrolysis.—The rate expres-

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[8] G. O. Pinching and R. G. Bates, *J. Res. Natl. Bur. Std.*, **40**, 405 (1948).

[9] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., New York, N. Y., 1943, p. 575.

TABLE I

EQUILIBRIUM QUOTIENTS AND RATE CONSTANTS FOR THE ACID HYDROLYSIS OF $[Pt(NH_3)_3Cl]^+$; NO CHLORIDE ADDED, *i.e.*, "b" = 0

Initial $[Pt(NH_3)_3Cl^+]$ "a," mM	Na_2SO_4, M	$NaClO_4$, M	Ionic strength "μ," M	Equilibrium titer 10 "T_∞," mM	Equilibrium quotient 10^4 K', M	Rate constants: k_{-1} M^{-1} sec.$^{-1}$	Rate constants: 10^5 k_1, sec.$^{-1}$
				For 25°			
1.00	0	0	0.0021	2.80	1.08	0.21	2.3
					0.88 ($\mu \doteq 0$)		
4.00	0	0	.0072	6.22	1.14	.21	2.4
					0.81 ($\mu = 0$)		
4.38	0	0	.0079	6.65	1.10	.19	2.3
					0.83 ($\mu = 0$)		
					Av. 0.84 ($\mu = 0$)	.20	2.3
1.00	0.1055	0	.318	3.74	2.30	.096	2.2
2.00	.1055	0	.318	6.08	2.65	.063	1.7
2.00	.0400	0.196	.318	6.20	2.78	.068	1.9
2.00	.0	.316	.318	6.62	3.20	.074	2.4
4.00	.1055	0	.318	9.13	2.70	.082	2.2
					Av. 2.7 ± 0.3	.073 ± 0.004	2.2 ± 0.3
				For 35°			
1.00	0	0	0.0021	2.82	1.10	0.69	7.6
					0.90 ($\mu = 0$)		
2.00	0	0.098	.100	6.25	2.84	.27	7.7
2.00	0	.316	.318	6.36	2.97	.26	7.7
2.00	0	.316	.318	6.64	3.30	.22	7.25
2.00	0	.316	.318	6.36	2.97	.26	7.7
2.00	0.010	.286	.318	6.64	3.30	.22	7.25
2.00	.02	.256	.318	6.31	2.90	.21	6.2
2.00	.035	.213	.318	5.98	2.55	.21	5.5
2.00	.070	.108	.318	5.81	2.40	.22	5.3
2.00	.080	.046	.318	5.95	2.52	.22	5.4
2.00	.1055	0	.318	5.81	2.40	.22	5.3
1.00	.1055	0	.318	3.65	2.10	...	...
4.00	.1055	0	.318	8.85	2.51	...	...
					Av. 2.7 ± 0.4 (μ = .318)	Av. .23 ± 0.02 (μ = .318)	Av. 6.6 ± 1.0

sions for the two reactions indicated in eq. 1 have been taken as

$$R_1 = k_1[Pt(NH_3)_3Cl^+] \tag{4}$$

$$R_{-1} = k_{-1}[Pt(NH_3)_3(H_2O)^{++}][Cl^-] \tag{5}$$

The solution of the kinetics is given by eq. 6 relating the titer, T, of a solution with the time, t.[4a]

$$\ln (T_\infty - T)[T_0 - T_\infty + \sqrt{(K' + b)^2 + 4K_1'a}]/(T_\infty - T_0)[T - T_\infty + \sqrt{(K' + b)^2 + 4K_1'a}] = -k_{-1}\sqrt{(K' + b)^2 + 4K_1'a}\; t \tag{6}$$

Titers of solutions were found to increase with time, and plots of the function in eq. 6 *vs.* time were represented satisfactorily by straight lines. Values of k_{-1} were calculated from the slopes of these lines, and k_1 was calculated from the expression

$$k_1 = k_{-1}K' \tag{7}$$

Rate constants generally could be duplicated to within about 10%. The experimental conditions for the rate determinations together with the indicated values of k_1 and k_{-1} also have been included in Table I. The acid hydrolysis rate constant, k_1, was found to be 2.2×10^{-5} sec.$^{-1}$ at 25°. The value for k_1 is somewhat larger than the value of 1.5×10^{-5} inferred from the rates of exchange by Banerjea, *et al.*,[5] but it is rather close to the rates of some first order substitution reactions, *e.g.*, with pyridine, which they observed. Although the equilibrium constant depends rather strongly upon ionic strength,

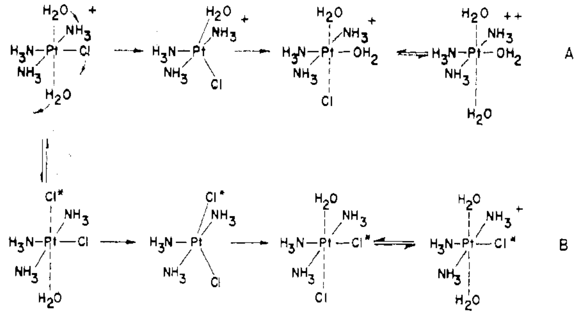

Fig. 2.—Possible mechanism for the substitution reactions of $[Pt(NH_3)_3Cl]^+$: A, acid hydrolysis; B, direct chloride exchange.

it is apparent that k_1 is independent of ionic strength, and the entire effect is reflected in k_{-1}. This feature also has been noted with $[PtCl_4]^{-2}$ and *trans*-$[Pt(NH_3)_2Cl_2]$, for which ionic strength variations have been studied. It is consistent with the formation of a transition state which has a +1 charge and with the reaction path that is shown in Fig. 2A. In this mechanism the square complexes are considered to have labile solvent ligands bonded at the axial positions and the configuration is therefore a distorted octahedron. The ligands at the axial positions also can be considered to be in labile equilibrium with other coördinating groups. In the acid hydrolysis, one of the axial H_2O molecules moves in to displace the chloride while one of the H_2O molecules is lost. The transition state therefore is assumed to be approximately a trigonal bipyramid.

Isotopic Exchange of the Chloride Ligand.—The isotopic exchange of chloride ion with the ligand was measured with Cl^{36} in solutions which were at chemical equilibrium with respect to the acid hydrolysis. The solutions usually were contained in flasks wrapped with opaque tape, although in a few instances exposure to the laboratory lights did not change results. At various times aliquots from an exchange solution were withdrawn for the determination of the specific activity in the chloride ligand. For the description of the isotopic exchange the terms below are defined following the practice in the earlier work.

u = concn. of Cl^{36} in $[Pt(NH_3)_3Cl]^+$, counts/min. l.
$U = u/[Pt(NH_3)_3Cl]$

The experimental procedure yielded the quantity U, and U/U_∞ represents F, the fraction of exchange. Some typical plots of log $(1 - F)$ *vs.* time appear in Fig. 3. It can be seen from the plots that any separation-induced exchange was negligible and that the plots were satisfactorily linear over periods of more than a half-life. The rate of exchange R_{ex} was calculated from the well known expression

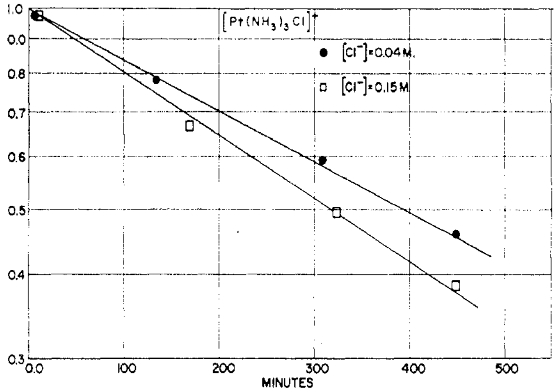

Fig. 3.—Typical exchange experiments: temperature 25°; $\mu = 0.318\ M$; $a = 1.75$ mmoles $[Pt(NH_3)_3Cl]^+$/l.

$$R_{ex} = (\ln 2)(a - T_\infty)(b + T_\infty)/\tau_{1/2}(b + a) \qquad (8)$$

Experimental conditions for the exchange experiments and the indicated half-times and exchange rates are given in Table II. The quantity $R_{ex}/(a - T_\infty)$ has been plotted as a function of chloride ion concentration in Fig. 4. At 25° experiments have been performed at two concentrations of the complex. The plot in Fig. 4 shows that the points follow along a straight line with an intercept on the ordinate satisfactorily close to k_1. Since a greater accuracy was possible with the exchange experiments than with the titrations, the values indicated for k_1 in Fig. 4 probably are better than those in Table I. The rate for the exchange can, therefore, be represented by the expression

$$R_{ex} = R_1 + R' = k_1[Pt(NH_3)_3Cl^+] + k'[Pt(NH_3)_3Cl^+][Cl^-] \qquad (9)$$

These results indicate that there is a substantial contribution from a process which is first order in both the complex and chloride. The value of k' is $7 \times 10^{-5}\ M^{-1}$ sec.$^{-1}$ at 25°. In this respect the $[Pt(NH_3)_3Cl]^+$ resembles *trans*-$[Pt(NH_3)_2Cl_2]$ in possessing such a chloride dependent exchange and differs from the other chloroammine complexes.

It now is possible to compare the behavior of the entire series of the chloride–ammonia complexes of platinum(II). Table III contains a compilation of equilibrium and rate constants for the acid hydrolysis and for the direct chloride exchange of this series of complexes, obtained in

TABLE II

EXCHANGE OF THE CHLORIDE LIGAND OF $[Pt(NH_3)_3Cl]^+$ IN EQUILIBRIUM SOLUTIONS

$[Pt(NH_3)_3Cl^+]$ Before aging "a," mM	$[Cl^-]$ Before aging "b," mM	$[Pt(NH_3)_3(H_2O)^{++}]$ calcd. 10 "T_∞," mM	Ionic strength "μ," M	Half-time of exchange, min.	Rate of exchange $10^8 R_{ex}$, M sec.$^{-1}$
			For 25°		
1.75	1.0	3.050	0.318[a]	263	3.04
1.75	10.0	0.430	.318[a]	364	4.65
1.75	40.0	.109	.318[a]	396	4.83
3.50	70.0	.124	.318[a]	352	10.90
1.75	100.0	.044	.318[a]	350	5.68
1.75	150.0	.029	.318[a]	317	6.30
1.75	40.0	.076	.043[c]	370	5.20
			For 35°		
1.75	10.0	0.500	0.100[b]	128.5	13.00
1.75	20.0	.220	.318[a]	130.0	14.10
1.75	40.0	.076	.043[c]	130.0	14.80
1.75	50.0	.095	.100[b]	124.0	15.70
1.75	80.0	.052	.318[a]	111.0	17.80
1.75	100.0	.050	.103[b]	106.0	18.70

[a] Added salt—Na_2SO_4. [b] Added salt—$NaClO_4$. [c] No added salt.

this Laboratory. Although k_1 is smallest for $[Pt(NH_3)_3Cl]^+$, in a rational comparison of the complexes the equilibrium and rate constants each need to be divided by n, the number of equivalent chlorides in the complex. Since $n = 1$ for $[Pt(NH_3)_3Cl]^+$, its chloride can be considered more labile than that of $[PtCl_4]^{-2}$, *cis*-$[Pt(NH_3)_2Cl_2]$, and at least part of the chloride of $[Pt(NH_3)Cl_3]^-$. Indeed, the small variation in acid hydrolysis rate constants for this series is its most striking feature and argues strongly against a simple dissociative mechanism.

The activation enthalpies, $\Delta H^\ddagger$, are all 19 kcal. within the reasonable experimental uncertainty of ±2 kcal. This feature is consistent with the mechanism illustrated in Fig. 2A in which the transition state forms *via* a similar intramolecular rearrangement for each complex together with the loss of a labile neutral solvent ligand. The acid hydrolysis kinetics appear to reflect very little "*trans*-effect" for the various complexes.

The direct replacement of chloride by chloride for the more negative complexes in a second order process cannot compete with replacement by the water in the presence of overwhelming quantities of solvent. However, it does become measurable for *trans*-$[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_3Cl]^+$. The low activation enthalpy of 19 kcal. and the corresponding high reaction rate of *trans*-$[Pt(NH_3)_2Cl_2]$ compared to 27 kcal. for $[Pt(NH_3)_3Cl]^+$ appear to be rather general for the substitution reactions other than acid hydrolysis. This direct exchange can occur by the mechanism of Fig. 2B, which is equivalent to that for the acid hydrolysis.

$[Pt(NH_3)Cl_3]^-$ is especially interesting since it contains non-equivalent chlorides, *i.e.*, a Cl^- *trans* to NH_3 and two equivalent chlorides *cis* to NH_3. It was shown that this ion undergoes acid hydrolysis with the k_1 and K_1' listed in Table III. However, exchange studies[4c] indicated that this acid hydrolysis did not account for the chloride exchange but that an additional exchange process occurred which also was chloride-independent, and that all

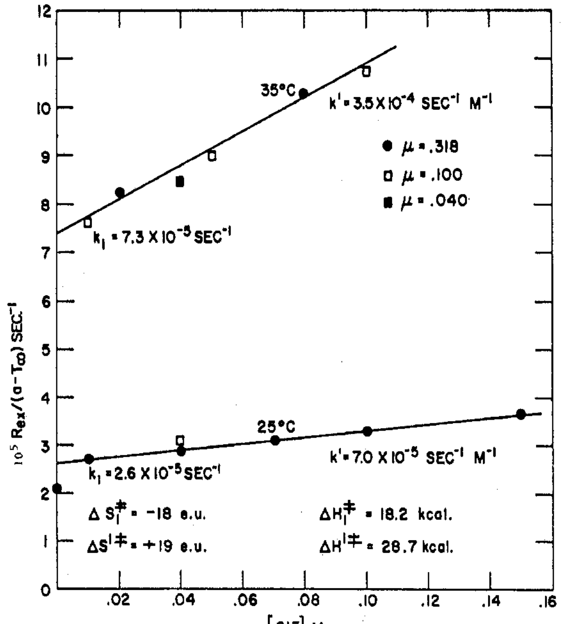

Fig. 4.—Chloride dependence of exchange rates.

TABLE III

EQUILIBRIUM AND RATE CONSTANTS OF THE CHLOROAMMINE COMPLEXES OF PLATINUM(II); TEMPERATURE 25°, $\mu = 0.318\ M$

Complex	Equil. quotients acid hydrolysis First $10^5 K_1'$	Second $10^5 K_2'$		Rate constants acid hydrolysis First $10^5 k_1$ sec.$^{-1}$	Second $10^5 k_2$ sec.$^{-1}$	Rate constant direct exchange of chloride ligand $10^6 k'$ sec.$^{-1}$ M^{-1}
$[PtCl_4]^{-2}$	1500	50		3.9	3.3	<3
$[Pt(NH_3)Cl_3]^-$ K_1'	1400	4	k_1	3.6	13	<3
K_1^*	<200		k_1^*	2.5		<3
cis-$[Pt(NH_3)_2Cl_2]$	330	40		2.5	3.3	~3
trans-$[Pt(NH_3)_2Cl_2]$	32	<2		9.8	<5	78
$[Pt(NH_3)_3Cl]^+$	27	...		2.6	...	7

three chlorides in the complex exchanged at comparable rates. The results could be explained by having one type of chloride undergo acid hydrolysis characterized by k_1 and K_1', and the other type with the rate constant designated by k_1^* and the upper limit for the equilibrium constant by K_1^* in Table III. Grinberg and Kukuskin[10] have expressed some concern that their first order rate constant of 6.0×10^{-5} sec.$^{-1}$ for the base hydrolysis of $[Pt(NH_3)Cl_3]^-$ has not agreed with our values of k_1. However, their value agrees very closely with the sum of the two rate constants $(k_1 + k_1^*) = (3.6 + 2.3) \times 10^{-5}$ sec.$^{-1}$, as it should if both types of chloride are replaced by OH^-. A tentative original assignment of k_1 and K_1' to the *cis*-chlorides was based on an apparent slight nonequivalence of the complexed chloride in a solution of the separated $[Pt(NH_3)(H_2O)Cl_2]$ toward chloride exchange and the OH^- substitution reaction.[4c] The systematics of the equilibrium constants for acid hydrolysis, now possible for the complete series of complexes, casts some doubt upon this assignment. In Fig. 5 has been plotted log K_1'/n for the complexes against the charge on the complexes. The points for the *cis*-$[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_3Cl]^+$, for which the replaced chloride is certainly *trans* to NH_3, define a line with a negative slope. The slope indicates a greater stability of the negative chloride ligand toward replacement by H_2O as the charge of the complex increases. The points for $[PtCl_4]^{-2}$ and *trans*-$[Pt(NH_3)_2Cl_2]$, with the replaced ligands certainly *trans*- to Cl^-, also determine a line with only a slightly smaller slope but which lies well below the other. For the general process of acid hydrolysis of a chloride ligand indicated in eq. 10, ΔF^0 increases about 1.0 kcal. for each

$$[L\text{-}Pt^{II}\text{-}Cl]^z + H_2O \longrightarrow [L\text{-}Pt^{II}\text{-}OH_2]^{z+1} + Cl^- \quad (10)$$

unit change in z, and ΔF^0 increases about 1.4 kcal. when L, the *trans*-ligand, is Cl^- rather than NH_3. The slope of the lower line may be reduced somewhat since *trans*-$[Pt(NH_3)_2Cl_2]$ is the only one of the complexes without an ionic charge or permanent dipole moment and it presumably will have a minimum interaction with the solvent.

Now the points for either log K_1' or log $K_1'/2$ for $[Pt(NH_3)Cl_3]^-$ lie close to the upper line, which would give a consistent picture if the

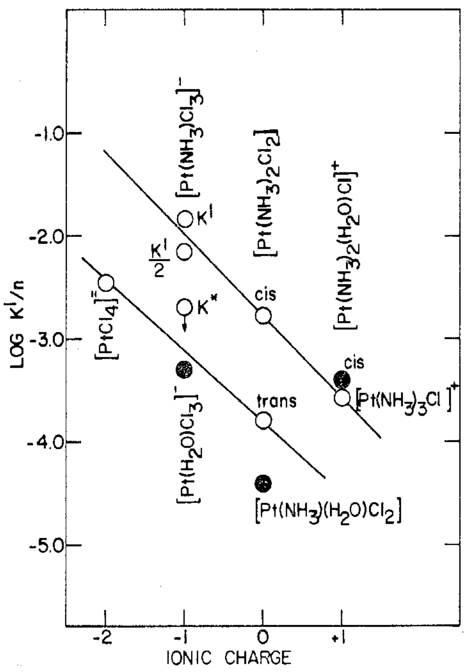

Fig. 5.—Dependence of the acid hydrolysis equilibrium rate constants upon the charge on the complex: ○, −log K_1'/n; ●, −log K' for the species indicated (these are equilibrium constants for a second acid hydrolysis of chloroammine complexes).

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[10] A. A. Grinberg and I. N. Kukuskin, *Zh. Neorg. Khim.*, **6**, 306 (1961).

chloride *trans* rather than *cis* to the NH_3 were replaced in the first acid hydrolysis. Only an upper limit for K^* can be given which lies somewhat above the lower line. Further support of this assignment is given by the magnitudes for the second acid hydrolysis constants which have been plotted in Fig. 5 as solid circles. It must be recognized that K_2 cannot be evaluated as accurately as K_1. For *cis*-$[Pt(NH_3)_2(H_2O)Cl]$, with the chloride *trans* to NH_3, the point falls close to the upper line; K_2' for *trans*-$[Pt(NH_3)_2Cl]$ was too small to measure. For $[Pt(H_2O)Cl_3]^-$, in which the chloride must be *trans* to either Cl^- or H_2O, the point falls close to the lower line. Hence, the effect of a *trans* H_2O apparently resembles that of Cl^- rather than NH_3. K_2' for $[Pt(NH_3)Cl_3]^-$ is exceptionally low and it falls somewhat below the lower line, consistent with the contention that the second chloride to be replaced is not *trans* to the NH_3. Furthermore, the high rate constant $k_2' = 13 \times 10^{-5}$ sec.$^{-1}$ for $[Pt(NH_3)(H_2O)Cl_2]$ would characterize the *trans*-isomer, a neutral species closely resembling the *trans*-$[Pt(NH_3)_2Cl_2]$, which also has a high rate constant. The apparent small non-equivalence in the substitution rates for the chloride ligand in solutions of $[Pt(NH_3)(H_2O)Cl_2]$ upon which the original assignment was based might have resulted from the presence of a small amount of the *cis*-isomer present together with the dominant *trans*-isomer. The lines in Fig. 5 predict the presence of 5–10% of the *cis*-isomer with a dominant *trans*-isomer. It will be most interesting, therefore, if some feasible means can be found for identifying unambiguously the predominant isomer formed by the acid hydrolysis of $[Pt(NH_3)Cl_3]^-$.

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The Identification of Some Cobalt(II) Ammine Azides

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X-Ray powder patterns and ammonia absorption studies characterize tbe cobalt(II) compounds formed by the thermal decomposition of $[Co(NH_3)_6](N_3)_3$ and by the reaction of cobalt(II) azide with gaseous ammonia. From the latter a crystalline diammine, an amorphous diammine, and a hexammine have been identified. A labile compound, possibly a diammine, has been recognized in mixtures. Two forms of cobalt(II) azide were found. The decompositions of $[Co(NH_3)_6](N_3)_3$ yield three different compounds, a tetrammine, a diammine, and an unidentified material occasionally observed in mixtures with the diammine.

Introduction

The thermal decomposition of solid $[Co(NH_3)_6](N_3)_3$ may yield cobalt(II) compounds.[1] Thus the products of the room temperature reaction of cobalt(II) azide with gaseous ammonia have been characterized and compared with the ammines yielded by $[Co(NH_3)_6](N_3)_3$.

Experimental

Preparation.—The preparation and decomposition of $[Co(NH_3)_6](N_3)_3$ has been described.[1] Cobalt(II) azide was prepared by the reaction of a 3% solution of hydrogen azide in ether[2] with cobalt(II) carbonate.[3] The very explosive, brown product was prepared in 0.3-g. lots, stored under ethereal HN_3, and protected from light.

Analysis.—The usual preparation yields two crystalline cobalt(II) azides and an unidentified, amorphous contaminant. Efforts to devise better methods of preparation or purification failed, necessitating considerable analytical efforts to establish beyond reasonable doubt the identity of the cobalt(II) azides. These were complicated by the lability of the sample to both hydrolysis and explosion.

The first samples were decomposed explosively in the vacuum line at 120 to 150°. Six runs gave N_2, 57.0 ± 1.8%; calcd. for $Co(N_3)_2$, 58.8%. The accuracy is within the limitations imposed by the small samples (10 to 20 mg.) and the system's volume; however, small quantities of H_2, 0.14 ± 0.04%, and HN_3, 0.3 ± 1%—identified by the approximate melting point, decomposition on sparking, and a red color reaction with aqueous ferric chloride—also were observed. Later efforts to determine cobalt iodometrically[4] or gravimetrically as the anthrani-

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[1] T. B. Joyner and F. H. Verhoek, *J. Am. Chem. Soc.*, **83**, 1069 (1961).

[2] L. F. Audrieth and C. F. Gibbs in H. S. Booth, "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Company, New York, N. Y., 1939, p.77.

[3] L. Wohler and F. Martin, *Ber.*, **50**, 586 (1917).

[4] H. A. Laitinen and L. W. Burdette, *Anal. Chem.*, **23**, 1268 (1951).