mmoles; in an entirely independent case, the corresponding values were 2.02 and 2.05 mmoles, respectively.

With respect to the role of $[Pt(en)(en\text{-}H)]^0$, the experiments involving this intermediate show that the decomposition of $[Pt(en)_2]^0$ is more complex than originally expected. The added complexity, however, arises from the unavoidable presence of excess potassium in the reaction mixture; this results in concurrent reactions that are not involved in the over-all reaction of $[Pt(en)_2]I_2$ with one equivalent of potassium since in this case the potassium is removed prior to the appearance of $[Pt(en)_2]^0$. Although $[Pt(en)(en\text{-}H)]$ undoubtedly appears in the reduction of $[Pt(en)_2]I_2$ with two equivalents of potassium before the excess potassium is removed by washing, the intermediate must react only slightly since after 3 to 4 hr. the final decomposition product, $[Pt(en\text{-}H)_2]^0$, is present to the extent of only about 10% of the Pt used originally as $[Pt(en)_2]I_2$. This interpretation is supported also by the persistence of the blue color at the end of the addition of potassium solution.

The unusual species derived from $[Pt(en)_2]I_2$ and reported in this and the preceding communication[2] may be summarized as

(1a) $[Pt(en)_2]I$ (2a) $[Pt(en)(en\text{-}H)]^0$
(1b) $[Pt(en)_2]^0$ (2b) $K[Pt(en)(en\text{-}H)]$

(3a) $[Pt(en)(en\text{-}H)]I$
(3b) $[Pt(en\text{-}H)_2]^0$
(3c) $K[Pt(en\text{-}H)(en\text{-}2H)]$

The complexes 1a and 1b contain platinum in the apparent 1+ and zero oxidation states. These products are unstable with respect to decomposition to elemental platinum and ethylenediamine at room temperature; at −33.5° they decompose with evolution of hydrogen and the formation of one or more of the basic complexes (3a, b, c). Although the dark red $[Pt(en)_2]I$ and the light pink $[Pt(en)_2]^0$ are both insoluble in liquid ammonia, their stabilities are of such a low order that evidence for their existence could be obtained only by analysis of their decomposition products.

The compounds 2a and 2b also contain platinum in their *apparent* 1+ and zero oxidation states, respectively, and their formation involves also the removal of a proton from a nitrogen atom in ethylenediamine coördinated with platinum. These are white ammonia-insoluble solids and evidence for their formation also was obtained through the study of their decomposition products.

The complexes 3a, 3b and 3c appear not only as decomposition products of (1a) and (1b) but also are formed by the interaction of $[Pt(en)_2]I_2$ with one, two and three equivalents of potassium amide. All three of these substances contain platinum in the 2+ oxidation state and although very hygroscopic, they are stable at room temperature in a dry inert atmosphere. Accordingly, these products were isolated, purified and subjected to direct analysis. Aqueous solutions of these products are strongly basic; this of course indicates the displacement of a proton from water. Both $[Pt(en)(en\text{-}H)]I$ and $[Pt(en\text{-}H)_2]^0$ are insoluble in liquid ammonia as well as in more than 20 common organic solvents.

Further studies on the structure of these unusual species are either in progress or are anticipated. Certain evidences suggest that at least some of these substances are polymeric; if so, the presence of platinum in 1+ and zero oxidation states may prove to be more apparent than real.

Austin, Texas

[Contribution No. 603 from the Institute for Atomic Research and Department of Chemistry, Iowa State College. Work was Performed in the Ames Laboratory of the U. S. Atomic Energy Commission]

Trichloroammineplatinate(II) Ion. Hydrolysis, Isotopic Exchange of Chloride and the *trans*-Effect

By Thomas S. Elleman, John W. Reishus and Don S. Martin, Jr.

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Rates of isotopic exchange between the chloride ligands in $[Pt(NH_3)Cl_3]^-$ and in the acid hydrolysis product, $[Pt(NH_3)Cl_2(H_2O)]$, with Cl^- have been determined in aqueous solutions in the temperature range 0–30°. For each complex the exchange occurs by the observable acid hydrolysis and by additional chloride-independent processes. It is proposed that the non-equivalent chlorides in each complex undergo separate acid hydrolyses. Although all such hydrolysis reactions have roughly the same rate constant and ΔH^*, there is considerable variation in ΔF^0. In support of this proposal, the substitution of chloride by hydroxide in $[Pt(NH_3)Cl_2(H_2O)]$ has been found by a tracer technique to be unsymmetric, indicating the presence of the *cis*-isomer. The mechanism of the acid hydrolysis reactions is discussed.

Introduction

The reaction of trichloroammineplatinate(II) ion with ammonia yields predominantly the *cis*-$[Pt(NH_3)_2Cl_2]$. This procedure for the preparation of the *cis*-isomer is one of the most frequently cited examples of the *trans*-effect which illustrates that a chloride ligand has a greater *trans*-directing influence than ammonia. By this means the isomer is formed which is less stable in a thermodynamic sense since it is converted upon heating into the *trans*-isomer.[1]

The authors have reported in an earlier publication[2] studies of the kinetics of the reversible acid hydrolysis of $[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Cl_2(H_2O)]$ in dilute solutions. The system was described by the reactions

$$[Pt(NH_3)Cl_3]^- + H_2O \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} [Pt(NH_3)Cl_2(H_2O)] + Cl^- \qquad (1)$$

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[1] A. V. Nikolaev, *Compt. rend. acad. sci. U.R.S.S.*, **20**, 571 (1938).

[2] T. S. Elleman, J. W. Reishus and D. S. Martin, Jr., This Journal, **80**, 536 (1958).

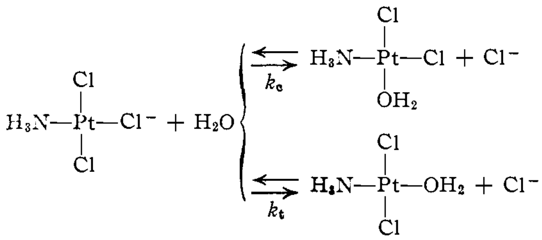
and

$$\mathrm{H_2O + [Pt(NH_3)Cl_2(H_2O)]} \underset{k_2}{\overset{k_{-2}}{\leftrightarrows}} \mathrm{[Pt(NH_3)Cl(H_2O)_2]^+ + Cl^-} \quad (2)$$

where for 25°

$k_1 = 3.6 \times 10^{-5}$ sec.$^{-1}$, $\Delta H_1\ddagger = 18.9$ kcal.
$k_{-1} = 2.5 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$, $\Delta H_1\ddagger = 16.8$ kcal.
$k_2 = 1 \times 10^{-5}$ sec.$^{-1}$
$k_{-2} = 0.2$ l. mole^{-1} sec.$^{-1}$

It was not possible by the earlier experiments to evaluate the stereochemical features of the reactions. The *trans*-effect predicts that the reaction to produce the *cis*-isomer occurs more rapidly, *i.e.*, $k_c > k_t$ for the reactions



$$\mathrm{H_3N{-}\overset{Cl}{\underset{Cl}{Pt}}{-}Cl^- + H_2O} \underset{k_c}{\leftrightarrows} \mathrm{H_3N{-}\overset{Cl}{\underset{OH_2}{Pt}}{-}Cl + Cl^-} \quad (1c)$$

$$\mathrm{H_3N{-}\overset{Cl}{\underset{Cl}{Pt}}{-}Cl^- + H_2O} \underset{k_t}{\leftrightarrows} \mathrm{H_3N{-}\overset{Cl}{\underset{Cl}{Pt}}{-}OH_2 + Cl^-} \quad (1t)$$

In the *cis*-$[\mathrm{Pt(NH_3)Cl_2(H_2O)}]$, of course, the two chlorides are non-equivalent, whereas in the *trans*-compound the chlorides are equivalent.

The present study was undertaken to determine the rate at which isotopically tagged chloride ion in the solution enters the various complexes. Reactions 1 and 2 offer a means by which such isotopic exchange with chloride can be accomplished. It is of interest to find whether additional means exist to permit the tagged chloride to enter the complexes. Under certain conditions the stereochemistry of reaction 1 may be resolved. If, for example, $k_c >> k_t$, two chlorides may approach isotopic equilibrium in $[\mathrm{Pt(NH_3)Cl_3}]^-$ much more rapidly than the third and *vice versa*. However, reaction 2 and its reverse may permit the exchange of the chloride which is not removed by the first hydrolysis (reaction 1). Also, a possibility exists that if the $[\mathrm{Pt(NH_3)Cl(H_2O)_2}]^+$ is exclusively the *trans*-complex, the chloride *trans* to the NH_3 will not exchange.

The hydrolysis of all the other mononuclear chloroammines of platinum(II) has been studied. Grantham, Elleman and Martin[3] found that $[\mathrm{PtCl_4}]^=$ undergoes acid hydrolysis but does not undergo additional isotopic exchange of chloride. However, $[\mathrm{PtCl_3(H_2O)}]^-$ undergoes a chloride exchange which is independent of chloride and which may possibly proceed *via* acid hydrolysis. Banerjea, Basolo and Pearson[4] found that *cis*-$[\mathrm{(Pt(NH_3)_2Cl_2}]$ undergoes an acid hydrolysis. Although they detected no hydrolysis product for *trans*-$[\mathrm{Pt(NH_3)_2Cl_2}]$ nor $[\mathrm{Pt(NH_3)_3Cl}]^+$, the isotopic exchange with chloride occurred by a process which was independent of chloride ion concentrations. Thus no exchange of chloride which is dependent on chloride concentration has yet been found for any of the complexes. The present complex is of special interest for it is the only one of the series which contains chloride *trans* to ammonia and other chloride *trans* to chloride.

Experimental

Materials.—$\mathrm{K[Pt(NH_3)Cl_3]}$ was prepared by the method described earlier.[2] $[\mathrm{Pt(NH_3)Cl_2(H_2O)}]$ was formed when solutions of $[\mathrm{Pt(NH_3)Cl_3}]^-$ were equilibrated with H_2O by reaction 1. Passage of dilute equilibrated solutions of $\mathrm{K[Pt(NH_3)Cl_3]}$ through a column of anion-exchange resin, Dowex 1, in the sulfate cycle, removed $[\mathrm{Pt(NH_3)Cl_3}]^-$ and Cl^-. The remaining $[\mathrm{Pt(NH_3)Cl_2(H_2O)}]$ solution was stored in concentrations not greater than 0.005 *M* at 0.0°. The equilibria in equations 1 and 2 were re-established but the species $[\mathrm{Pt(NH_3)Cl_2(H_2O)}]$ comprised approximately 85% of the total platinum. The remainder was mostly $[\mathrm{Pt(NH_3)Cl(H_2O)_2}]^+$.

Tetraphenylarsonium acetate, $\mathrm{(As(C_6H_5)_4)(C_2H_3O_2)}$, was prepared by passing the $\mathrm{(As(C_6H_5)_4)Cl}$ reagent, purchased from the Hach Chemical Co., through a Dowex 1 anion-exchange resin in the acetate cycle. The effluent solution was standardized gravimetrically by the precipitation of $\mathrm{(As(C_6H_5)_4)(ClO_4)}$. When the acetate reagent was added to equilibrated solutions of $\mathrm{K[Pt(NH_3)Cl_3]}$, the compound $\mathrm{(As(C_6H_5)_4)[Pt(NH_3)Cl_3]}$ precipitated quickly. For the analyses of these precipitates, samples which had been dried at 95° were weighed and dissolved in hot water. An excess of $\mathrm{LiClO_4}$ was added, and the $\mathrm{(As(C_6H_5)_4)(ClO_4)}$ which precipitated was filtered and weighed. The platinum and NH_3 analyses of the filtrate followed the procedures used for the $\mathrm{K[Pt(NH_3)Cl_3]}$ samples.[2] Results: $\mathrm{(As(C_6H_5)_4)^+} = 53.7$, calcd. 54.5; Pt = 27.2, calcd. 27.7; NH_3 = 2.5, calcd. 2.4. Chloride was not determined since Cl-analyses of $\mathrm{K[Pt(NH_3)Cl_3]}$ were generally of rather poor precision.[2] However, a $\mathrm{(As(C_6H_5)_4)NO_3}$ solution, *p*H 4.65, was added to a solution of 0.01 *M* $\mathrm{K[Pt(NH_3)Cl_3]}$, *p*H 4.60, which had been aged for 20 hr. The *p*H after the precipitation of $\mathrm{(As(C_6H_5)_4)[Pt(NH_3)Cl_3]}$ was 4.65. Therefore no appreciable amount of $\mathrm{(As(C_6H_5)_4)[Pt(NH_3)Cl(OH)]}$, which would reduce the *p*H, could have precipitated.

Chlorine-36, half-life 3.1×10^5 years, decaying by a single 0.72 Mev. β-disintegration, was the tracer isotope. The radioactive chlorine, carried in dilute HCl, was obtained from the Isotopes Division, U.S.A.E.C., Oak Ridge, Tennessee.

Water for the preparation of all solutions was drawn from the distilled water tap and was redistilled from alkaline permanganate.

Platinum normally was recovered as the metal by a formate reduction and reused in the experiments. A neutron-activation analysis indicated an iridium content of 20 p.p.m.

Other reagents which were used met A.C.S. specifications.

Equipment.—Reaction temperatures were maintained to ±0.1° by a Sargent constant temperature bath. At 0°, however, ice-baths were used. For other experiments below 20° the water cooling coil of the thermostat bath was replaced by a refrigeration coil.

Radioactivity Measurements.—The rather conventional procedures for preparing, weighing, mounting and counting radioactive samples were described by Grantham, *et al.*[3] The practice of carrying several filter papers through the washing, drying and weighing procedure was continued to provide corrections for humidity differences in the counting sample tares.

For each sample the specific activity, S cts./min. mg. Cl, was always determined from the counting rate, corrected to standard geometry and self-scattering conditions, from the weight of the deposit and from its chloride content. Such specific activities were proportional to the disintegration rates per mole of chloride.

Exchange in Aged Solutions of $\mathrm{K[Pt(NH_3)Cl_3]}$ and KCl.—The proper quantities of $\mathrm{K[Pt(NH_3)Cl_3]}$, KCl and $\mathrm{Na_2SO_4}$ to give solutions with the desired concentrations and an ionic strength of 0.318 molar were weighed into a volumetric flask, and water was added to the mark. The flasks usually were wrapped with opaque tape to exclude light and were thermostated at the reaction temperature for a sufficient time to approach closely equilibrium with respect to the hydrolysis reactions 1 and 2. Aliquots were withdrawn at intervals, and a fivefold excess of $\mathrm{(As(C_6H_5)_4)(C_2H_3O_2)}$ was added immediately to each aliquot to precipitate the $[\mathrm{Pt(NH_3)Cl_3}]^-$. After 4 min. the aliquot was filtered. The precipitates were washed three times with H_2O and

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(3) L. F. Grantham, T. S. Elleman and D. S. Martin, Jr., THIS JOURNAL, **77**, 2965 (1955).

(4) D. Banerjea, F. Basolo and R. G. Pearson, *ibid.*, **79**, 4055 (1957).

allowed to stand overnight. The $(As(C_6H_5)_4)[Pt(NH_3)Cl_3]$ was deposited in an even, reproducible film on the filter paper, and its specific activity S was determined. To obtain S_∞ for each reaction, at least two aliquots were taken after a sufficient time so that no further change in the specific activity was detectable. These data provided a fraction of exchange for the $[Pt(NH_3)Cl_3]^-$ species defined as S/S_∞. In a few experiments with high chloride concentrations, the initial specific activity of the tracer-chloride was carefully determined, but this information was not generally required.

In aged solutions, for which the chloride concentration was low (less than 0.02 M), $[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Cl_2(H_2O)]$ were present in comparable concentrations. The addition of Ag_2SO_4 to the solutions quickly precipitated AgCl and $Ag[Pt(NH_3)Cl_3]$. However, a drop in pH followed the addition of Ag_2SO_4, which indicated the coprecipitation of significant amounts of insoluble $Ag[Pt(NH_3)Cl_2(OH)]$. The precipitation of this compound was suppressed by the addition of H_2SO_4 to lower the pH to *ca.* 2. At pH 2 the addition of Ag_2SO_4, 20–30% in excess of the amount calculated to precipitate Cl^- and $[Pt(NH_3)Cl_3]^-$, removed these anions effectively. The major portion of the $[Pt(NH_3)Cl_2(H_2O)]$ remained in the filtrate after filtration through a glass sinter. The filtrate was treated with excess aqueous NH_3 and heated for 4 hr. at 80° to replace the chloride ligands by NH_3. The solution then was acidified with H_2SO_4 and Ag_2SO_4 was added. The resulting AgCl precipitate was collected on a filter paper, dried, weighed and counted. With a careful control of the amount of Ag_2SO_4 which was initially added, this *silver-ion scavenging* procedure provided the specific activity of the $[Pt(NH_3)Cl_2(H_2O)]$ species. Without such information analysis of the exchange would have been severely curtailed.

Exchange in Fresh Solutions of $K[Pt(NH_3)Cl_3]$ and KCl.—For fresh solution exchange the proper quantities of KCl and Na_2SO_4 were dissolved in water of a predetermined volume and temperature. A weighed quantity of $K[Pt(NH_3)Cl_3]$ then was dissolved in the solution and the chloride tracer was added immediately. At this time only negligible quantities of the hydrolyzed species were present. From this point the experiment was treated in the same fashion as the aged-solution experiments.

Chloride Exchange with $[Pt(NH_3)Cl_2(H_2O)]$.—Dilute solutions of $[Pt(NH_3)Cl_2(H_2O)]$, prepared by the ion-exchange method, were transferred to reaction flasks, and Na_2SO_4 was added to bring the ionic strength to 0.318 mole/l. The flasks were stored for a period in the thermostat. The following concentrations of a typical preparation at 20°, after the hydrolysis equilibria 1 and 2 were reëstablished, were calculated from the equilibrium constants: $[Pt(NH_3)Cl_2(H_2O)] = 20.2 \times 10^{-4}\ M$, $[Pt(NH_3)Cl(H_2O)_2{}^+] = 3.4 \times 10^{-4}\ M$, $[Pt(NH_3)Cl_3{}^-] = 0.4 \times 10^{-4}\ M$, and $(Cl^-) = 2.5 \times 10^{-4}\ M$. Enough solid KCl was added to increase the Cl^- concentration by an increment of $29.0 \times 10^{-4}\ M$. The solution approached an equilibrium state in which $[Pt(NH_3)Cl_2(H_2O)] = 20.0 \times 10^{-4}\ M$, $[Pt(NH_3)Cl(H_2O)_2{}^+] = 0.4 \times 10^{-4}\ M$, $[Pt(NH_3)Cl_3{}^-] = 3.6 \times 10^{-4}\ M$ and $(Cl^-) = 26.0 \times 10^{-4}\ M$. Initially, the $[Pt(NH_3)Cl(H_2O)_2]^+$ concentration decreased very rapidly, but the $[Pt(NH_3)Cl_3]^-$ formed slowly with a period of approximately 14 hr. at 20°.

Approximately 1 hr. after the addition of the KCl, the chloride tracer was added. Solution aliquots were withdrawn after various time intervals. The specific activity of the chloride ligands then was determined by the *silver-ion scavenger* procedure described above.

In some experiments the Cl^{36} tracer was included with the KCl which was added to increase the chloride ion content of the equilibrated $[Pt(NH_3)Cl_2(H_2O)]$ solutions. The specific activity of complexed chloride increased more rapidly in these experiments by virtue of the reverse of reaction 2. From the increase in the initial slope of S/S_∞ the rate of replacement of H_2O in $[Pt(NH_3)Cl(H_2O)_2]^+$ by chloride was estimated. A value 0.16 M^{-1} sec.$^{-1}$ was indicated for k_{-2} at 20°, in satisfactory agreement with the earlier rough estimate of 0.2 for 25°.

Substitution of NO_2^- and OH^- in $[Pt(NH_3)Cl_2(H_2O)]$.—Experiments were performed to detect a possible nonequivalence of the chloride ligands in $[Pt(NH_3)Cl_2(H_2O)]$. $[Pt(NH_3)Cl_2(H_2O)]$ was allowed to exchange with tracer chloride for a short period of time (1–2 hr.). The exchange was then quenched by the addition of Ag_2SO_4. The average specific activity of the chloride ligands in a portion of the solution was obtained by the *silver-ion scavenging* procedure. Various amounts of either KNO_2 or KOH were added to other portions of solution. With KOH, Ag_2O formed quickly and was filtered off. The platinum complex was transformed to the anion $[Pt(NH_3)Cl_2(OH)]^-$ and OH^- slowly replaced Cl^-. The reaction of NO_2^- with $[Pt(NH_3)Cl_2(H_2O)]$ proceeded more rapidly. After a fraction of the chloride ligands had been replaced, the solution was acidified to pH 2, and Ag_2SO_4 was added to precipitate the free chloride. These precipitates were separated by filtration, and their specific activities were determined. The chloride ligands which had passed into the filtrate were recovered by the ammonia replacement method used in the *silver-ion scavenging* procedure.

Results

Exchange for $[Pt(NH_3)Cl_3]^-$ in Aged Solutions.—Preliminary experiments were intended to establish the number of chlorides in $[Pt(NH_3)Cl_3]^-$ which exchanged with chloride ion. The exchange solutions contained high chloride ion concentrations with a known specific activity. The specific activity of the $[Pt(NH_3)Cl_3]^-$ fraction was determined after several days. If two chloride ligands had exchanged, the final specific activity, $S_\infty(2)$ will be

$$S_\infty(2) = 2bS_s^0/3\,(b + 2a) \qquad (3)$$

where

a = initial concn. of $[Pt(NH_3)Cl_3]^-$, M
b = initial concn. of Cl^-, M
S_s^0 = initial specific activity of Cl^-, cts./min. mg. Cl

If all three chloride ligands had exchanged, the final specific activity will be

$$S_\infty(3) = bS_s^0/(b + 3a) \qquad (4)$$

The results, shown in Table I, clearly indicate that all three ligands had undergone exchange.

TABLE I

EXCHANGE OF CHLORIDES IN $[Pt(NH_3)Cl_3]^{-a}$

Initial $[Pt(NH_3)Cl_3{}^-]$ (a) M	Initial chloride (b) M	Time, hr.	$S_\infty(2)$ calcd.	$S_\infty(3)$ calcd. cts./min. mg. Cl	S obsd.
0.0083	0.134	144	65	93	97.8 ± 1.6
					96.9 ± 1.6
					94.2 ± 1.5
					96.7 ± 1.6
.0166	.075	100	51	66	65.2 ± 1.0
					65.4 ± 1.0

[a] Temp. = 20°; S_s^0 = 109 ± 4 cts./min. mg. Cl.

A series of exchange experiments were performed with aged solutions at several temperatures to determine whether the acid hydrolysis equilibrium rates measured earlier[2] were sufficient to account for the exchange. The conditions of the various experiments have been included in Table II. The detailed results of two typical experiments are shown in Fig. 1, one for high chloride concentration and one for low chloride. In this figure the usual exchange variable log $(1 - S/S_\infty)$ is plotted against the time. The initial points of this variable, 1.0 ± 0.03, indicate no exchange induced by the separation process. It is also apparent from the figure that all three chloride ligands have exchanged at approximately the same rate. This feature implies that the *trans effect* does not apply for the exchange process. Deviations of the plots of the exchange variable, log $(1 - S/S_\infty)$, *vs.* time from linearity were not large, and the time of half-exchange serves as a convenient parameter to characterize the exchange rate. Observed values of the time of half exchange are included in Table I. A few of the experiments in Table I were repeated several times and the results were satisfactorily reproducible.

TABLE II

EXCHANGE BETWEEN $[Pt(NH_3)Cl_3]^-$ AND Cl^- IN AGED SOLUTIONS[a]

Temp., °C.	Initial $[Pt(NH_3)Cl_3^-]$ concn. × 10^2, M	Initial Cl^- concn., M	Equilibrium $[Pt(NH_3)Cl_2(H_2O)]$ concn. × 10^3, M	Aging time, hr.	pH	Time of half-exchange for $[Pt(NH_3)Cl_3]$ Obsd. hr.	Calcd. hr.
0.0	1.66	0.0100	6.76	117		48	50
	0.830	.134	0.65	117		159	139
15.0	1.66	.0100	7.26	42		8.0	8.1
20.0	1.66	.0100	7.45			4.3	4.4
				42		4.0[b]	
				50	5.58	5.1[c]	
				49	5.41	4.9[d]	
				42	0.90	4.5[e]	
				30	3.92	0.02[f]	
	1.66	.025	5.30	34		6.2	6.1
	1.66	.050	3.48	34		9.5	7.7
	1.66	.075	2.57	34		9.5	9.2
	1.66	.268	0.933	40	6.58	13.0	13.2
	.830	.201	.55	40	5.96	14.0	13.7
	.830	.268	.41	42	6.02	14.5	14.5
	.415	.0100	2.23	42	4.89	9	7.9
25.0	1.66	.0100	7.59	12	5.01	3.2	2.8
	0.830	.134	0.82	12	6.10	7.2	7.4
30.0	1.66	.0100	7.72	24	5.51	1.8	1.8
	0.830	.134	0.85	24	6.19	4.5	4.6

[a] Na_2SO_4 added to give ionic strength to 0.318 except where noted. [b] Exchange solution exposed to room light. [c] No Na_2SO_4 added, ionic strength was 0.0266. [d] Na_2SO_4 added to give ionic strength of 0.080. [e] No Na_2SO_4 added, H_2SO_4 added to give the low pH. [f] $(NH_4)_2Ce(NO_3)_6$ added, 5 × 10^{-4} mole/l.

Since in aged solutions equilibrium with respect to the acid hydrolysis was established, rates of these reactions can be expressed by the equations

$$R_1 = k_1[Pt(NH_3)Cl_3^-] = R_{-1} = k_{-1}[Pt(NH_3)Cl_2(H_2O)][Cl^-] \quad (5)$$

and

$$R_2 = k_2[Pt(NH_3)Cl_2(H_2O)] = R_{-2} = k_{-2}[Pt(NH_3)Cl(H_2O)_2^+][Cl^-] \quad (6)$$

where the brackets denote molar concentrations of the indicated species. Since the experiments in Fig. 1 indicated that all the chloride ligands in $[Pt(NH_3)Cl_3]^-$ exchanged at approximately equivalent rates, the kinetic expressions were set up initially on the basis that the three chloride ligands in $[Pt(NH_3)Cl_3]^-$ were equivalent and the two chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ were equivalent. The following symbols were defined for this treatment

s = concn. of Cl^{36} in Cl^- (cts./min. l.)
u = concn. of Cl^{36} in $[Pt(NH_3)Cl_3]^-$ (cts./min. l.)
v = concn. of Cl^{36} in $[Pt(NH_3)Cl_2(H_2O)]$ (cts./min. l.)
w = concn. of Cl^{36} in $[Pt(NH_3)Cl(H_2O)_2]^+$ (cts./min. l.)
$I = s + u + v + w$ = concn. total Cl^{36}
$S_s = s/[Cl^-]$ specific activity of chloride ion
$S_u = u/3[Pt(NH_3)Cl_3^-]$
$S_v = v/2[Pt(NH_3)Cl_2(H_2O)]$
$S_w = w/[Pt(NH_3)Cl(H_2O)_2^+]$

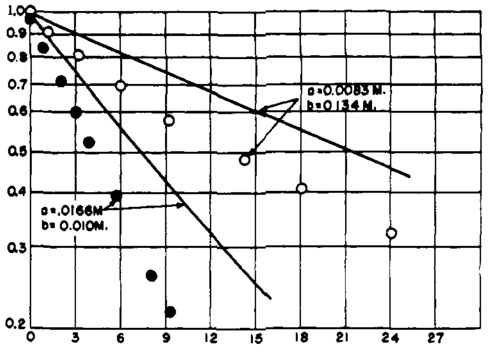


Fig. 1.—Exchange between $[Pt(NH_3)Cl_3]^-$ and Cl^- in aged solutions. Temp. = 20°, ionic strength = 0.318 M, $a = [Pt(NH_3)Cl_3^-]$ before aging and $b = [Cl^-]$ before aging. Smooth curves represent the calculated extent of exchange if the only exchange means are the first and second acid hydrolyses reactions, characterized by k_1, k_{-1}, k_2 and k_{-2}, and if the chloride ligands in each complex are equivalent.

For exchange *via* only the acid hydrolysis equilibria, these rate equations apply

$$du/dt = -R_1(3S_u) + R_{-1}(2S_v + S_s) \quad (7)$$

$$dv/dt = R_1(2S_u) - R_{-1}(2S_v) - R_2(2S_v) + R_{-2}(S_s + S_w) \quad (8)$$

$$dw/dt = R_2(S_v) - R_{-2}(S_w) \quad (9)$$

In any of the experiments of Table II the largest concentration of $[Pt(NH_3)Cl(H_2O)_2]^+$ was less than 0.1% of $[Pt(NH_3)Cl_3^-]$. Therefore to a very good approximation $w << u$, $dw/dt << du/dt$ and $S_w = S_v$. With these approximations, equations 7 and 8 become linear differential equations in the two independent variables u and v, for which the solutions are

$$(S_\infty - S_u)/S_\infty = A_1e^{-\alpha_1t} + A_2e^{-\alpha_2t} \quad (10)$$

$$(S_\infty - S_v)/S_\infty = B_1e^{-\alpha_1t} + B_2e^{-\alpha_2t} \quad (11)$$

where A_1, A_2, B_1, B_2, α_1 and α_2 are functions of the equilibrium concentrations of the species and the four rate constants for reactions 1 and 2.

The curves plotted in Fig. 1 for the two experiments represent the calculated solution, equation 10, for each of the experiments. It was clear that the hydrolysis reactions, characterized by k_1, k_{-1}, k_2 and k_{-2}, are not sufficiently rapid to account for the rate at which Cl^{36} enters the $[Pt(NH_3)Cl_3]^-$. Similar results were obtained for every experiment listed in Table II. Some additional exchange process must therefore be postulated to explain the observed results. Two possible processes have been considered in modifications to equations 7 and 8.

$$du/dt = -R_1(3S_u) + R_{-1}(2S_v + S_s) + R'(S_s - S_u) \quad (12)$$

$$dv/dt = R_1(2S_u) - R_{-1}(2S_v) - R_2(2S_v) + R_{-2}(S_w + S_s) + R''(S_s - S_v) \quad (13)$$

The reaction rate R' describes an exchange process involving $[Pt(NH_3)Cl_3]^-$ and R'' describes a process for $[Pt(NH_3)Cl_2(H_2O)]$. The experiments in Fig. 1 show a distinct difference from the behavior of $[PtCl_4]^=$. For $[PtCl_4]^=$ the exchange rate under high chloride concentrations corresponded just to the acid hydrolysis; hence direct exchange for $[PtCl_4]^=$, equivalent to reaction R', was negligible.

For $[Pt(NH_3)Cl_3]^-$, further experiments were required to characterize the rate processes R' and R''.

Exchange of $[Pt(NH_3)Cl_3]^-$ in Fresh Solutions.—When the KCl with the Cl^{36}-tracer was added to freshly prepared solutions of $K[Pt(NH_3)Cl_3]$, the activity entered the complex with an initially rapid rate. The data from one such experiment are shown in Fig. 2. It was necessary for these experiments to be conducted with low chloride concentrations so that the acid hydrolysis equilibrium state would not be approached too rapidly. The results in Fig. 2 were analyzed in the following way. For initial concentrations of $[Pt(NH_3)Cl_3^-] = a$, and $[Cl^-]$ (with tracer) $= b$, the initial rate of formation of $[Pt(NH_3)Cl_2(H_2O)]$ is given by equation 5 to be

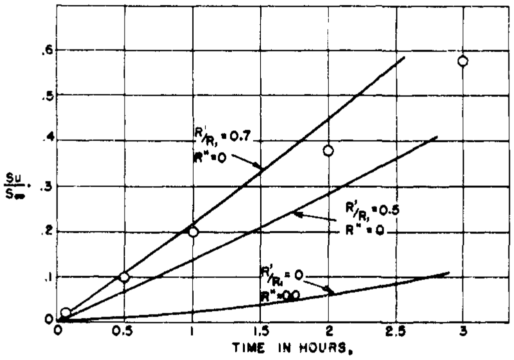


Fig. 2.—Exchange between $[Pt(NH_3)Cl_3]^-$ and Cl^- in the freshly prepared solutions. Temp. = 20°, ionic strength = 0.318 *M*. Initial $[Pt(NH_3)Cl_3^-] = 1.66 \times 10^{-2}$ *M*, initial $[Cl^-] = 5.00 \times 10^{-3}$ *M*.

$$d[Pt(NH_3)Cl_2(H_2O)]/dt = k_1a (\text{for } t = 0) \qquad (14)$$

For short times, therefore, its concentration is given approximately by

$$[Pt(NH_3)Cl_2(H_2O)] = k_1at \qquad (15)$$

For the period that equation 15 is valid, equation 12 becomes

$$du/dt = k_{-1}[Pt(NH_3)Cl_2(H_2O)]b(2S_v) + k_{-1}[Pt(NH_3)Cl_2(H_2O)]I + R'(I/b) \qquad (16)$$

After the concentration of $[Pt(NH_3)Cl_2(H_2O)]$ from equation 15 has been substituted into equation 16, integration for the case in which $R' = 0$ and $S_v = I/b$ (*i.e.*, $R''/R = \infty$) yields

$$u = 3k_1k_{-1}at^2/I2 \qquad (17)$$

Equation 17 has been used to plot the curve for S/S_∞ labeled $R' = 0$, $R'' = \infty$ in Fig. 2. It is seen that exchange of $[Pt(NH_3)Cl_2(H_2O)]$ alone cannot account for the rate at which chloride activity enters the complex, and some exchange of $[Pt(NH_3)Cl_3]^-$ was required.

Integration of equation 16 for the case that $S_v = 0$ gives

$$u = \frac{k_1k_{-1}at^2I}{2} + R'It/b \qquad (18)$$

This approximation is very satisfactory for values of S_u/S_∞ up to 0.2 to 0.3. The values of S/S_∞ obtained from equation 18 have been plotted for $R' = 0.7R_1 = 0.7k_1a$ and for $R'_1 = 0.5R_1 = 0.5k_1a$. In a set of experiments, of which Fig. 2 is one example, with initial Cl^- concentrations varying from 0.005 to 0.075 *M*, the indicated ratio R'/R was independent of $[Cl^-]$ and amounted to 0.5–0.7. Therefore the direct exchange of $[Pt(NH_3)Cl_3]^-$ is chloride independent, *i.e.*, R_1 is given by the equation

$$R' = k'[Pt(NH_3)Cl_3^-] \qquad (19)$$

where $k' = 0.5–0.7k_1$.

Exchange for $[Pt(NH_3)Cl_2(H_2O)]$ in Aged Solutions of $K[Pt(NH_3)Cl_3]$.—Figure 3 illustrates the results of exchange in an aged solution of $K[Pt(NH_3)Cl_3]$ with low chloride concentration for which the specific activity of the chloride ligands in $[Pt(NH_3)Cl_2(H_2O)]$ was followed as a function of time. The low specific activities of the initial points indicated that the separation procedure was satisfactory and that no separation-induced exchange occurred. The specific activity for the $[Pt(NH_3)Cl_2(H_2O)]$ increased rapidly. The lower curve, D, indicates the function predicted for the growth of S_v if there was no exchange process for $[Pt(NH_3)Cl_2(H_2O)]$ other than the second acid hydrolysis reaction. Curve A was calculated for a value $(k'' + k_2)/k_{-1}(Cl^-) = 3$. This ratio gave the curve which was considered to be the most satisfactory fit to the initial slope indicated by the experimental points. The calculated curve for specific activity in $[Pt(NH_3)Cl_3]^-$, shown by curve C, was not changed appreciably for values of $k''/k_{-1}(Cl^-)$ between 0 and 4.

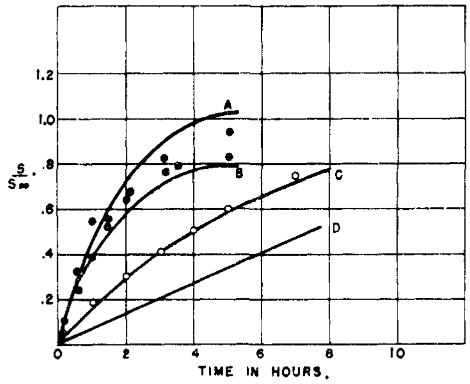
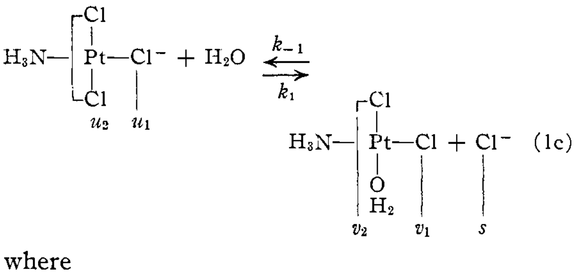


Fig. 3.—Exchange between $[Pt(NH_3)Cl_3]^-$, $[Pt(NH_3)Cl_2(H_2O)]$ and Cl^- *vs.* time for aged solutions. Temp. = 20°, ionic strength = 0.318 *M*, $[Pt(NH_3)Cl_3^-]$ before aging = 1.66×10^{-2} *M*, $[Cl^-]$ before aging = 0.0100 *M*. $[Pt(NH_3)Cl_2(H_2O)]$ (equilibrium) = 0.00745 *M*. ○ obsd. S/S_∞ $[Pt(NH_3)Cl_3]^-$; ● obsd. S/S_∞ $[Pt(NH_3)Cl_2(H_2O)]$; A, calcd. S_v/S_∞ for $R'/R_1 = 0.7$, $R''/R_1 = 3$; B, calcd. S_v/S_∞ for $R'/R_1 = 0.7$, $R''_1 = 0$, $R_2''/R_1 = 3.0$; C, calcd. S_u/S_∞ for $R'/R_1 = 0.7$, $R'' = 3.0$; D, calcd. S_v/S_∞ for $R'/R_1 = 0.7$; $R'' = k_2[Pt(NH_3)Cl_2(H_2O)]$.

It is interesting to note that this calculated curve for S_v, as can be seen in Fig. 3, slightly overshoots the infinite-time value, S_∞. This calculated curve deviates from the experimental points by approximately 10–15% at 3–4 hr. Such deviation is not large in view of the difficulties and the uncertainty in the procedure. However, the experiments were repeated carefully several times and the results appeared consistent and reproducible.

The small inconsistency of the calculated and experimental points suggested that possibly the chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ were not equivalent and might exchange at different rates. The results of Banerjea, Basolo and Pearson[4] with $[Pt(NH_3)_3Cl]^+$ and with *trans*-$[Pt(NH_3)_2Cl_2]$ showed that exchange of chloride ligands sometimes takes place under conditions in which the presence of the hydrolysis product is not detectable. The possibility therefore was considered in which the two chlorides *cis* to the ammonia in $[Pt(NH_3)Cl_3]^-$ underwent the acid hydrolysis reaction (1c) but *trans*-chloride exchanged by the reaction R′, which was similar to the exchange reaction of $[Pt(NH_3)_3Cl]^+$ and *trans*-$[Pt(NH_3)_2Cl_2]$. The two chlorides in the *cis*-$[Pt(NH_3)Cl_2(H_2O)]$ are then no longer equivalent. A description of the kinetics of exchange has now become a 4-variable problem for which the following treatment is given.



(1c)

where

u_1 = concn. of Cl^{36} *trans* to the NH_3 in $[Pt(NH_3)Cl_3]^-$, cts./min. l., etc.

S_{u_1} = $u_1/[Pt(NH_3)Cl_3^-]$, specific activity of the Cl^- *trans* to the NH_3 in $[Pt(NH_3)Cl_3]^-$, etc.

If the chloride *trans* to NH_3 in $[Pt(NH_3)Cl_2(H_2O)]$ does not undergo exchange by any process, including hydrolysis, rate expressions (20) to (23) can be written to replace equations 12 and 13

$$du_1/dt = -R_1S_{u_1} + R_{-1}S_{v_1} + R'(S_s - S_{u_1}) \qquad (20)$$

$$du_2/dt = -2R_1S_{u_2} + R_{-1}(S_s + S_{v_2}) \qquad (21)$$

$$dv_1/dt = R_1S_{u_1} - R_{-1}S_{v_1} \qquad (22)$$

$$dv_2/dt = R_1S_{u_2} - R_{-1}S_{v_2} + R''(S_s - S_{v_2}) \qquad (23)$$

In these equations $R_1 = R_{-1}$ for steady state conditions, and the rate constants k_1 and k_{-1} are just those of the first acid hydrolysis. The acid hydrolysis of $[Pt(NH_3)Cl_2(H_2O)]$ has been included as a part of R''. The solution of this set of differential equations has been obtained by an electronic analog computer. The computer solution for the experimental conditions of Fig. 3 has been included for the case of $R' = 0.70R_1$ and $R''/R_1 = 3.0$. This solution gives the same initial slope for the specific activity in $[Pt(NH_3)Cl_2(H_2O)]$ as the solution in which the chloride ligands in each complex were considered to be equivalent. However, for longer times, the 4-variable solution drops below the other. It lies somewhat closer to and indeed slightly below most of the experimental points. The experiments imply therefore that the two chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ are not equivalent, that both undergo exchange, but one of the chloride exchange processes is much faster than the other.

Chloride Exchange of $[Pt(NH_3)Cl_2(H_2O)]$.—The exchange experiments for solutions of $[Pt(NH_3)Cl_2(H_2O)]$, which had been prepared by the ion-exchange procedure, were designed to test the conclusion of the last section. Figure 4 shows the experimental results which were obtained. For the more general case the differential equations 22 and 23 must be modified to give

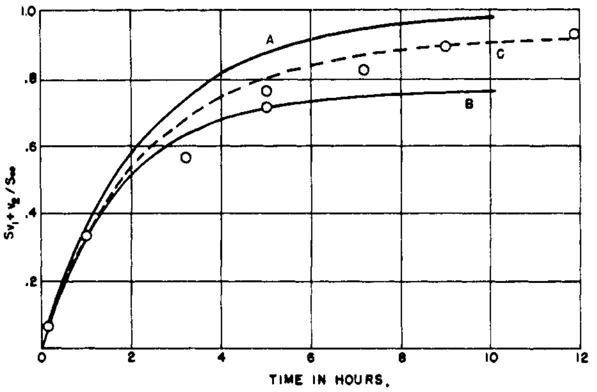


Fig. 4.—Exchange between $[Pt(NH_3)Cl_2(H_2O)]$ and Cl^- *vs.* time. Temp. = 20°, ionic strength = 0.318 *M*. Equilibrated solution of $[Pt(NH_3)Cl_2(H_2O)]$, total Pt = 24.0 × 10^{-4} *M* to which KCl was added to increase Cl^- by 2.90 × 10^{-3} *M*. 1 hr. before initiation of exchange. A, calcd. for $k_1'' = k_2'' = k''/2 = 9k_{-1}[Cl^-]$ — (equivalent chlorides); B, calcd. for $k_1'' = 0$; $k_2'' = k'' = 18k_{-1}[Cl^-]$; C, calculated for $k_2'' = 4k_1'' = 4/5k'' = 14.4k_{-1}[Cl^-]$.

$$dv_1/dt = R_1S_{u_1} - R_{-1}S_{v_1} + R_1''(S_s - S_{v_1}) \qquad (24)$$

$$dv_2/dt = R_1S_{u_2} - R_{-1}S_{v_2} + R_2''(S_s - S_{v_2}) \qquad (25)$$

so that different exchange rates of the two chlorides can be considered. The differential equations 20, 21, 24 and 25 were solved for the conditions that a steady state had been obtained and that $[Pt(NH_3)Cl_3^-] << [Pt(NH_3)Cl_2(H_2O)]$. These conditions were not attained exactly but provided a satisfactory approximation for a convenient solution.

Curve A in Fig. 4 is the solution for the case in which

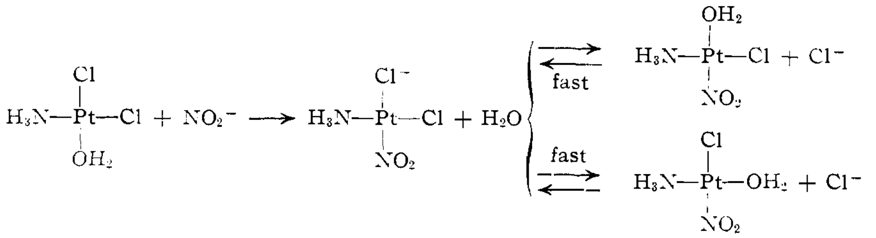
$$R_1'' = k_1''[Pt(NH_3)Cl_2(H_2O)] \qquad (26)$$

and

$$R_2'' = k_2''[Pt(NH_3)Cl_2(H_2O)] \qquad (27)$$

where $k_1'' = k_2''$. This solution corresponds to equivalent chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ which undergo an exchange by a process which is zero order in chlorides. The k_1'' and k_2'' have been set equal to $k''/2$, which was used to plot curve A in Fig. 3. Curve B in Fig. 4 is the solution for which $k_1'' = 0$ and $k_2'' = k''$ (which was used to calculate curve B in Fig. 3). Curve A in Fig. 4 approaches S_∞ rapidly, for both chlorides exchange directly. Curve B approaches the asymptotic value much more slowly, since the chloride *trans* to NH_3 (v_1) can only exchange by the R′ reaction in $[Pt(NH_3)Cl_3]^-$. A period of *ca.* 56 hr. was calculated for the long component of curve B in Fig. 4. Again, the experimental points fall between the two extremes. Curve C of Fig. 4, which was selected as the best fit to the experimental points, corresponds to a solution in which $k_2'' = 4k_1'' = {}^4/_5k'' = 14.4k_{-1}[Cl^-]$. It was noted that k_1'' corresponds closely (within 40%) to the estimate given previously for k_2.

Substitution Reactions of $[Pt(NH_3)Cl_2(H_2O)]$.—The exchange kinetics indicated that the chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ were not equivalent, so additional evidence for this conclusion was sought,



$$H_3N\text{—}\underset{OH_2}{\overset{Cl}{Pt}}\text{—}Cl + NO_2^- \longrightarrow H_3N\text{—}\underset{NO_2}{\overset{Cl^-}{Pt}}\text{—}Cl + H_2O \left\{ \begin{array}{l} \underset{\text{fast}}{\rightleftarrows}\ H_3N\text{—}\underset{NO_2}{\overset{OH_2}{Pt}}\text{—}Cl + Cl^- \\ \overset{\text{fast}}{\rightleftarrows}\ H_3N\text{—}\underset{NO_2}{\overset{Cl}{Pt}}\text{—}OH_2 + Cl^- \end{array}\right. \qquad (28)$$

The substitution of chloride by NO_2^- and OH^- was effected in complexes which had undergone a partial exchange of the chloride ligands with the tracer chloride ion. The results of the hydroxide-substitution reactions are in Table III. In every experiment the specific activity of the replaced chloride lay below the specific activity of the chloride which remained in the complex. The differences in specific activity were not large, but they appeared to be distinctly greater than the experimental uncertainty. The low specific activity of the replaced chloride samples might be caused by the coprecipitation of a platinum compound with the AgCl. However, analysis of the AgCl deposits by the colorimetric procedure of Ayres and Meyer[5] indicated less than 5% of the platinum content which would have been required to give the observed results.

TABLE III

SUBSTITUTION OF Cl^{-*} IN PARTIALLY EXCHANGED $[Pt(NH_3)Cl_2(OH)]^-$ BY OH^-

$$\text{Temp.} = 20°;\ \underset{\text{A}}{[Pt(NH_3)Cl_2(OH)]^-} + OH^- \rightarrow \underset{\text{B}}{[Pt(NH_3)Cl(OH)_2]^-} + \underset{\text{C}}{Cl^-}$$

Exchange time for $[Pt(NH_3)Cl_2(H_2O)]$ and Cl^{*-} hr.	OH^- substitution time, hr.	Chloride wt. in AgCl ppts. mg. Cl: Replaced Cl^- fraction "C"	Chloride wt. in AgCl ppts. mg. Cl: Retained fraction "B"	Chloride wt. in AgCl ppts. mg. Cl: Total "A"	Specific activity, cts./min. mg. Cl: Replaced Cl^- fraction "C"	Specific activity, cts./min. mg. Cl: Retained fraction "B"	Specific activity, cts./min. mg. Cl: Total "A"
1.3	1.8	4.1	11.4	7.9	242	276	280
	2.0	4.8	11.3		236	289	
	3.5	5.7	10.2		245	281	
	3.5	5.9	10.2		263	287	
1.2	1.0	2.1	11.9	7.6	311	352	352
	2.0	3.1	11.3	5.1	280	358	
3.25	1.0	3.1	20.8		569	640	
	2.0	5.1	17.8		482	615	

Some additional features of the nitrite substitution were noted. The substitution of one NO_2^- per Pt did not reduce the acid content of the solution substantially, although the potentiometric titrations indicated the presence of a slightly stronger acid. When Ag_2SO_4 in limited excess was added to precipitate the substituted chloride, the weights of precipitated AgCl were higher than the amounts corresponding to the substitution. With the addition of the Ag_2SO_4, the acid content of the solution increased immediately. When two NO_2^- per Pt had reacted there was a substantial reduction in the acid equivalents of the solution. It was still possible to precipitate at least two equivalents of chloride. The observations were consistent with the substitution reactions 28. The addition of a second NO_2^- group would give predominantly $[Pt(NH_3)Cl(NO_2)_2]^-$. The labilizing of the chlorides for acid hydrolysis upon the addition of nitrite provides for the rapid isotopic equilibration of the complexed chlorides.

Discussion

The rate constants which have been indicated by this work are included in Table IV. It is interesting to note that if only the activity of $[Pt(NH_3)Cl_3]^-$ is followed, one cannot detect a non-equivalence for the chlorides. The constants k' and k'' in Table IV are substantially the "trial and error" values which were considered to give the best description for the exchange of $[Pt(NH_3)Cl_3]^-$ in its aged solutions under the assumption that the chlorides in each complex are equivalent. The values for τ_{calcd} (time of half exchange in Table II) were computed from the finally selected values of k' and k''. The calculations demonstrate that the exchange reactions of $[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Cl_2(H_2O)]$ must occur overwhelmingly by processes which are zero order in chloride. The results in Table II also show that the exchange rates are nearly independent of ionic strength. The exchange behavior is not affected by H^+ so long as the pH was less than *ca.* 4.5–5.0, for which the concentration of the conjugate bases of the aquo-complexes are negligible. In the few cases that the exchange was followed in glass flasks exposed to the laboratory light, there was no increase in the exchange rate. The presence of cerium(IV) in low concentrations appeared to accelerate enormously at least a portion of the exchange, and this phenomenon deserves further study. With the sum of the rate constants $k_1'' + k_2''$ equal to k'', the calculated initial slope for the specific activity in Fig. 4 is identical for the cases of equivalent or non-equivalent chlorides. It is recognized that the behavior predicted for the unsymmetric chlorides was not greatly different from the equivalent-chloride model in view of the experimental difficulties and uncertainties.

TABLE IV

SUMMARY OF RATE CONSTANTS

Temp., °C.	$k_1{}^a$ (k_{1c}) $\times 10^{+5}$, sec.$^{-1}$	$k_{-1}{}^a$ $\times 10^3$, M^{-1} sec.$^{-1}$	k' $(k_{1t}?)$ $\times 10^5$, sec.$^{-1}$	k_{-2} $\times 10^3$, M^{-1} sec.$^{-1}$	k'' $\times 10^5$, sec.$^{-1}$	k_1'' $(k_2?)$ $\times 10^5$, sec.$^{-1}$	k_2'' $\times 10^5$, sec.$^{-1}$
0.0	0.21	0.19	0.11		0.69	0.11	0.58
15.0	1.3	0.98	0.65				
20.0	2.4	1.7	1.2	0.16	8.9	1.8	7.1
25.0	3.6	2.5	2.5	0.2[a]			
30.0	5.8	3.8	4.1		20	4	16
ΔH^* (kcal.)	18	17	20		18	19	18

[a] From reference 2.

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[5] G. H. Ayres and A. S. Meyer, Jr., *Anal. Chem.*, **23**, 299 (1951).

A non-equivalence of chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ requires that at least a portion of this species be the *cis*-isomer. A significant simplification results if it is assumed that the *cis*-isomer forms predominantly. The rate constant k_1 becomes the rate constant k_{1c}, and k' is assigned to k_{1t}. Since $k_{1t}/k_1 = 0.5–0.7$ over the temperature range, the predominance of the *cis*-isomer results from the feature $k_{-1t} >> k_{-1c}$. Such a conclusion requires the *cis*-isomer in aqueous solution to be the more stable in a thermodynamic sense, which is somewhat unexpected in view of the relative stability of the solid *cis*- and *trans*-dichlorodiammineplatinum(II) isomers. However, a difference of only 3 kcal. in the stability between the isomers will explain the results; in aqueous solution the stability of the *cis*-isomer will be enhanced by its larger dipole moment. Some contribution to stability for the *cis*-isomer also arises from the greater π-bonding, which is possible for the two chlorides. The π-bonding has been proposed to account for the positive ΔH^0 in the conversion of the *cis*-bis-(triethylphosphine)-dichloroplatinum(II) ion into the *trans*-isomer, reported by Chatt and Wilkins.[6] The rate constant k_1'' can be associated with k_2, and k_2'' can represent the rate of an acid hydrolysis reaction for which the rate constant of the reverse reaction is very much greater than k_{-2}. All of the exchange which has been observed can therefore occur by acid hydrolysis, the replacement of chloride by the solvent. An interchange of the rate constants k_1'' and k_2'' leads to substantially the same exchange results and therefore this alternative is a possibility. If the non-equivalence of chlorides were due to the simultaneous existence of comparable quantities of the *cis*- and *trans*-isomers, at least a comparable stability for the two isomers would be required. Furthermore, an additional process, which is first order in $[Pt(NH_3)Cl_3^-]$, independent of chloride, but which is not an acid hydrolysis, would have to be postulated to account for the exchange characterized by k'.

With the present work and the earlier experiments,[3,4] there are now nine reactions for mononuclear complexes of platinum(II), containing only H_2O, NH_3 and Cl^- ligands, in which the exchange of chloride has been demonstrated to occur by either a measurable acid-hydrolysis equilibrium or by a process which is zero order in chloride ion. Apparently the direct, S$_N$2 type of replacement of ligand-chloride by the ion cannot compete with the substitution by the solvent. For all nine reactions, the first-order rate constants at 25° fall within the narrow range of 1×10^{-5} to 8×10^{-5} sec.$^{-1}$, despite the fact that the charges on the complex species range from -2 to $+1$. From the temperature dependence of the rate constants k_1, k', k_1'' and k_2'', it is apparent that the energies of activation for the processes differ by not more than 3 kcal./mole from one another. The general rule can be stated that a H_2O ligand in the platinum(II) complexes is replaced by a substituting group more rapidly than Cl^- which in turn is replaced more rapidly than NH_3.

All of the information concerning the system is consistent with the proposal of Banerjea, Basolo and Pearson[4] that substitution reactions of platinum(II) complexes proceed by a mechanism in which bond formation must accompany the bond breaking. They suggested that a dissociative mechanism can account for the processes. They proposed mechanism A in Fig. 5 as a general substitution reaction in which two molecules, which are weakly bonded to the Pt along the tetragonal axis of the complex, move in toward the central atom as the ligand is lost. In the transition state the five ligands have approximately a trigonal bipyramid arrangement, the equatorial plane for which includes the entering group, the *trans*-ligand (L) and a solvent molecule. However, the microscopic reversal of this mechanism will constitute an alternative substitution mechanism. As a consequence, for any single substitution, not only path A must be considered in Fig. 5 but also B which is equivalent to the reverse of A. With any particular conjugate substitution pair the reaction might take place predominantly by one or the other of the two paths, depending on the relative energy of the two alternative transition states. In some cases both mechanisms might make comparable contributions.

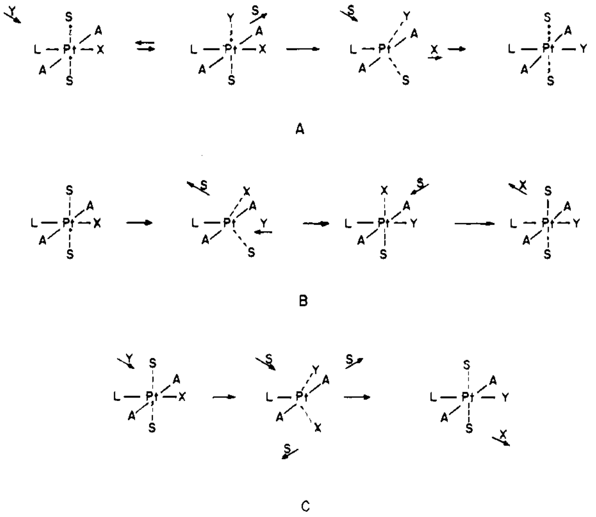

Fig. 5.—Mechanism for substitution reactions in which Y replaces X which is *trans* to *L'*. A, proposal by Banerjea, Basolo and Pearson.[4] B, alternative to A required by principle of microscopic reversibility; C, S$_N$2 mechanism.

In view of this complication the S$_N$2 mechanism illustrated as C in Fig. 5 appears more attractive. For this mechanism the transition state for a substitution process is symmetrical for the leaving and entering group. This transition state was utilized by Orgel[7] and by Chatt, *et al.*,[8] to account for the *trans*-effect. Since this transition state also is stabilized by π-bonding to Y as well as by L, it also accounts for the feature noted by Banerjea, Basolo and Pearson[4] that the rates of substitution increase with *trans*-directing character. Substitutions for chloride which are zero order in the substitution group can occur by the acid hydrolysis followed by the second-order replacement of the aquo-ligand.

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(6) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 273 (1952).

(7) L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956).

(8) J. Chatt, L. A. Duncanson and L. M. Vananzi, *J. Chem. Soc.*, 4456 (1955).

The formation of the *cis*-$[Pt(NH_3)_2Cl_2]$ by the reaction of NH_3 with $[Pt(NH_3)Cl_3]^-$ may not be a direct substitution of ammonia for chloride. The high yield of the *cis*-isomer probably reflects the relative competition of chloride and ammonia to replace H_2O in the *cis*- and *trans*-$[Pt(NH_3)Cl_2(H_2O)]$, both of which exist in the solutions in their equilibrium concentrations. However, the direct substitution of NH_3 in $[Pt(NH_3)Cl_3]^-$ by a slow second-order process is not precluded.

The experimental work has indicated considerable differences in the ΔF^0 for the acid hydrolysis of chloride ligands in the Pt^{II} complexes. Because of these differences the concentrations of some hydrolysis products escape detection, despite the fact that all the hydrolysis reactions occur at nearly the same rates. No simple correlation of the stability of the various complexes toward the acid hydrolysis with total ionic charge, the nominal charge distribution in the complex, or a geometrical arrangement of the groups to maximize the extent of π-bonding has appeared. Yet it appears that a satisfactory explanation for the stabilities of the various complexes must be presented before a satisfactory description of the substitution processes can be given.

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AMES, IOWA

[CONTRIBUTION NO. 2381 FROM THE GATES AND CRELLIN LABORATORIES, CALIFORNIA INSTITUTE OF TECHNOLOGY; AND FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Molecular Configuration of Dicobalt Hexacarbonyl Diphenylacetylene

BY W. G. SLY[1]

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The configuration of dicobalt hexacarbonyl diphenylacetylene has been determined by X-ray crystal structure analysis and is reported at a preliminary stage of refinement. The crystals are monoclinic with $a = 16.01$ Å., $b = 15.94$ Å., $c = 8.015$ Å. and $\beta = 107.6°$. There are four molecules in a unit cell of space group $Cc-C_s^4$. The molecule has sixfold coördination about the cobalt atoms in a distorted octahedral configuration with the C–C bond of the acetylene approximately normal to the Co–Co bond in a distorted tetrahedral arrangement that gives approximate C_{2v} symmetry for the molecule, except for the benzene rings. The molecule can be related to the proposed structures of dicobalt octacarbonyl, which are based upon a trigonal bipyramidal system of bonds, by considering the bonds from the cobalt atoms to the acetylenic linkage as metal atom–π bonds similar to those found for the palladium chloride complexes with ethylene.

The compound dicobalt hexacarbonyl diphenylacetylene, $(CO)_6Co_2[C_2(C_6H_5)_2]$, hereinafter referred to as DHDPA, is derived from dicobalt octacarbonyl through the replacement of two $C\equiv O$ groups by the hydrocarbon ligand in a reaction that is quite general for alkynes.[2,3] Dicobalt octacarbonyl, like most of the transition metal carbonyls, is active as a catalyst for introducing H_2 and/or $C\equiv O$ into organic molecules and DHDPA can be regarded as simply a stable intermediate formed in a typical reaction of this type.[4] The structure of DHDPA, determined through X-ray analysis and reported here at a preliminary stage of refinement, represents one of the first molecules to be studied which exhibit a multi-point attachment of a single organic molecule to more than one metal atom, possibly analogous to the postulated attachment of an organic substrate to a metal surface at more than one point during heterogeneous catalytic reactions.[5,6] In the structure of DHDPA we have definite structural evidence in support of such a theoretical model.

DHDPA forms dark purple crystals which are found to be monoclinic with the lattice parameters

$$\begin{aligned} a &= 16.01 \text{ Å.} \\ b &= 15.94 \text{ Å.} \\ c &= 8.015 \text{ Å.} \\ \beta &= 107.6° \end{aligned}$$

These lattice parameters coupled with the measured density give an experimental value for the number of molecules per unit cell of $z = 3.82$ ($z = 4$). Systematic absences require the space group to be either C2/c or Cc, and, although the crystal morphology and the absence of any measurable piezoelectric effect favor the holohedry, the structure has been determined to occupy the space group $Cc-C_s^4$, which has no positions of symmetry.

Complete X-ray intensity data were obtained for DHDPA with equi-inclination Weissenberg techniques using iron Kα X-radiation. The structure has been solved and refined by straightforward methods of X-ray analysis, all in three dimensions *viz.*, a Patterson function, a Fourier synthesis based on the cobalt atoms alone, three cycles of least-squares refinement and a difference-Fourier synthesis in which the cobalt atoms were subtracted. All of the atoms of the structure are well resolved in the electron density maps and although the structure is not completely refined the configura-

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(4) H. W. Sternberg and I. Wender, private communication.

(5) B. M. W. Trapnell, "Chemisorption," Butterworths Scientific Publications, London, 1955, p. 218 *et seq.*

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