complex is near the "magnetic crossover point" where the ground state changes from a singlet to a triplet and population of both levels is possible. The fact that the bromide complex remains diamagnetic is a clear indication that the ligand field strength of the iodide ion is greater in this system too.

These data concur with the arguments for assignment of the first spin-allowed visible band in the spectra of these five-coordinate cations to the $^1A_1 \rightarrow {}^1B_2$ transition. In further support of this assignment is the fact that these bands occur at higher energy in water than they do in nonaqueous solvents. In water the axial perturbation caused by the halide ions is decreased relative to that in weaker solvating media such as acetone because of the competition between the solvent and the substrate for the anions. As a result the energy of the d_{z^2} orbital is much less affected and the $^1A_1 \rightarrow {}^1B_2$ transition occurs at higher energy.

A further aspect of the spectra of these five-coordinate $Ni(DPES)_2X^+$ cations must be noted since it may indicate a tendency of the nickel ion to increase its coordination number from five to six. When progressively larger amounts of lithium chloride are added to a solution of $Ni(DPES)_2(ClO_4)_2$ in acetone, the frequency of maximum absorption shifts to lower energy (24,040 → 20,000 cm^{-1}), and the extinction coefficient passes through a maximum of about 700 at 21,500 cm^{-1}. This maximum occurs at the 1:1 equiv point and is therefore believed to be characteristic of the five-coordinate $[Ni(DPES)_2Cl^+]$ species. A similar effect is observed in the spectra of the bromo and iodo complexes as the absorption bands of $[Ni(DPES)_2Br](ClO_4)$ and $[Ni(DPES)_2I](ClO_4)$ are shifted from 20,490 to 19,380 cm^{-1} and 20,000 to 18,450 cm^{-1}, respectively, when excess bromide and iodide ions are added. In the latter case the band at 18,450 cm^{-1} is identical with that observed in the spectrum of $Ni(DPES)_2I_2$, and, since it is asymmetric to the high-energy side, it could be indicative of an equilibrium mixture of five- and six-coordinate species. This would be a plausible interpretation of the effects of excess halide on the spectra of the analogous five-coordinate bromo and chloro complexes also.

Acknowledgment.—This work was supported in part by a Frederick Gardner Cottrell Grant from Research Corporation and a National Aeronautics and Space Administration Traineeship for J. F. S. We also wish to thank Dr. M. A. Robinson for obtaining the Nujol spectrum and for helpful discussions.

CONTRIBUTION FROM THE MATERIAL SCIENCE AND CHEMISTRY DEPARTMENT,
NAVAL POSTGRADUATE SCHOOL, MONTEREY, CALIFORNIA 93940

Kinetics of the Consecutive Substitutions of Ammonia by Chloride Ion in Tetraamminepalladium(II) Ion[1]

BY RICHARD A. REINHARDT AND ROBERT K. SPARKES

Received June 9, 1967

The reaction of $Pd(NH_3)_4^{2+}$ with Cl^- in acid solution follows predominantly the course

$$Pd(NH_3)_4^{2+} \xrightarrow{k_A'} Pd(NH_3)_3Cl^+ \xrightarrow{k_B'} trans\text{-}Pd(NH_3)_2Cl_2$$

Each pseudo-first-order rate constant is found to obey the two-term rate law $k' = k_1 + k_2[Cl^-]$. Values found at 25° and $\mu = 1$ are $k_{A1} = 0.0011$ sec^{-1}, $k_{A2} = 0.0071\ M^{-1}$ sec^{-1}, $k_{B1} = 9 \times 10^{-4}$ sec^{-1}, and $k_{B2} = 0.030\ M^{-1}$ sec^{-1}. Activation enthalpies are smaller than for corresponding Pt(II) reactions; activation entropies are all negative. Estimate is made of the rate constants of the very slow step leading to $Pd(NH_3)Cl_3^-$: at 30°, $k_{C1} \sim 3 \times 10^{-6}$ sec^{-1} and $k_{C2} \sim 4 \times 10^{-6}\ M^{-}$ sec^{-1}. The *trans* and *cis* effects are discussed.

Introduction

Substitution reactions of square-planar platinum(II) complexes have been studied extensively and results have been summarized elsewhere.[2] Characteristics of these reactions to be noted here are two-term rate laws, *trans* and *cis* effects, and negative entropies of activation. The rates of reaction of analogous Pt(II) and Pd(II) complexes[3] have been studied and it was found that the relative reactivity of Pd to Pt is *ca.* 10^5, presumably as a result of the increased tendency of Pd(II) to form the five-bonded intermediate.

In their studies of the substitution of various ligands into $Pd(acac)_2$ (acac = acetylacetonate), Pearson and Johnson[4] have established the fundamental similarity in the behavior of the complexes of the two metals. In particular, the two-term rate law was found and a very large *trans* effect was observed.

---

[1] This research has been supported by the Office of Naval Research. Portions are taken from the M.S. Thesis of R. K. Sparkes, Naval Postgraduate School, 1966.

[2] (a) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 388 (1962); (b) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 2; (c) U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

[3] F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

[4] R. G. Pearson and D. A. Johnson, *ibid.*, **86**, 3983 (1964).

The present study is an investigation of the kinetics of the change taking place when hydrogen and chloride ions are added to a solution of tetraamminepalladium(II) ion. The principal reaction is

$$\mathrm{Pd(NH_3)_4^{2+} + 2H^+ + 2Cl^- = Pd(NH_3)_2Cl_2 + 2NH_4^+}$$

Further substitution to $\mathrm{Pd(NH_3)Cl_3^-}$ and $\mathrm{PdCl_4^{2-}}$ is extremely slow compared to the main reaction. The use of the previously reported equilibrium data[5] permits selection of reaction conditions to ensure homogeneity and completeness of reaction and to avoid significant formation of aquated by-products. As a result of this study it is possible to examine further the qualitative similarities and the quantitative differences between the reactions of Pd(II) and Pt(II) complexes.

Experimental Section

Materials.—Pd(II) complexes were prepared and analyzed as described previously.[5]

Equipment.—Absorbance data were taken on a Beckman Model DU spectrophotometer provided with a thermostated cell holder. Matched 10-cm cylindrical cells were used throughout. It was found necessary to provide insulation around the 10-cm cell compartment to avoid temperature drifts. The reference solution for each run was of identical composition to the sample save for the omission of Pd complex.

Measurements of pH were made with a Beckman Research Model pH meter.

Kinetics.—Stock solutions were prepared containing 0.5–0.7 m*M* $\mathrm{Pd(NH_3)_4^{2+}}$, *ca.* 0.01 *M* ammonia, the desired quantity of sodium chloride (ammonium chloride in a few runs), and sodium perchlorate for adjustment of ionic strength. For the pH–time measurements the electrodes were immersed in a sample of stock held in the constant-temperature bath and to this system was added a carefully controlled excess of dilute hydrochloric acid (also at bath temperature). For absorbance–time measurements perchloric acid (to make 0.05–0.1 *M*) was added to an aliquot of stock and the solution was promptly transferred to the absorbance cell; the first point could be taken 25–40 sec after mixing. For either type of experiment, data were taken until only a very slow change was occurring. Runs consisted of 20–40 points.

Most of the absorbance data were obtained at 326 and 355 mμ. The first of these corresponds roughly to the $\mathrm{Pd(NH_3)_4^{2+}}$–$\mathrm{Pd(NH_3)_2Cl_2}$ isosbestic and is close to the wavelength maximum for $\mathrm{Pd(NH_3)_3Cl^+}$; the second is at the $\mathrm{Pd(NH_3)_3Cl^+}$–$\mathrm{Pd(NH_3)_2Cl_2}$ isosbestic. The spectrum of the product, after about 15 min of reaction, agreed quite satisfactorily with that of a freshly prepared solution of solid *trans*-$\mathrm{Pd(NH_3)_2Cl_2}$ in the region 310–400 mμ. Below 310 mμ, however, the solution of the solid showed a steady decrease in absorbance with decreasing wavelength, whereas the product of the kinetic runs showed a sharp increase. This effect is believed to be due to the formation of small quantities of $\mathrm{Pd(NH_3)Cl_3^-}$, the strong ultraviolet band of which begins in this region. Because of this observation, a few runs were made at 290 mμ to examine the rate of this process.

Results

Treatment of the Data.[6]—At 355 mμ, where absorbance, A, is nearly proportional to $[\mathrm{Pd(NH_3)_4^{2+}}]$, log $(A_\infty - A)$ was found to be almost linear with time. At 326 mμ ($\Delta A \propto [\mathrm{Pd(NH_3)_3Cl^+}]$), log $(A - A_\infty)$ passed through a maximum and reached a linear behavior at long times with a slope equal to that of the corresponding 355-mμ runs. The observed behavior is consistent with the reaction scheme

$$\mathrm{Pd(NH_3)_4^{2+}} \xrightarrow{k_A'} \mathrm{Pd(NH_3)_3Cl^+} \xrightarrow{k_B'} \mathrm{Pd(NH_3)_2Cl_2} \qquad (1)$$

where k_A' and k_B' are the observed, first-order rate constants[7] (*i.e.*, first order with respect to complex). From a plot of the 355-mμ data, k_A' can be approximated and both constants can be found graphically from the 326-mμ data by using substantially the method described by Ashley and Hamm.[8] These approximate values were used to initiate the least-squares fits to be described below.

It was apparent from the graphical analysis that the value selected for one rate constant affected that found for the other. The relative sensitivity index, $(k_B'/k_A')(dk_A'/dk_B')$, was found to be approximately 1–1.5 for absorbance runs at 326 mμ, 0.05–0.1 for those at 355 mμ, and 0.2 for the pH runs. As a consequence, k_B' could be determined reliably only from the 326-mμ data and the resulting average was used to generate k_A' for corresponding 355-mμ or pH runs. (For a number of pH runs it was necessary to estimate k_B' by interpolation.)

The pH data[6] and the absorbance data for which ionic strength was not controlled (*i.e.*, $\mu = [\mathrm{Cl^-}]$) were analyzed by least-squares fit[9] using the integrated form of the rate equations[10] corresponding to eq 1. Five parameters (four, when k_B' was fixed) were determined for each run: the rate constants, the preexponential rate factors[6] (functions of rate constants and extinction coefficients), and the infinity value of absorbance or $[\mathrm{H^+}]$.

The absorbance data[6] from solutions of unit ionic strength were analyzed by the Guggenheim[10] method, employing

$$E - E' = I_A e^{-k_A' t} + I_B e^{-k_B' t} + I_C \qquad (2)$$

where E and E' are[11] absorbance per centimeter at times t and $t + \Delta$, where Δ is set arbitrarily equal to the reciprocal of the first approximation for k_A'. I_C is a small correction for the slow growth of $\mathrm{Pd(NH_3)Cl_3^-}$, estimated from a few experiments run to very long times (see below). This correction was equivalent to no more than 0.001 in measured absorbance. Rate constants and the preexponential factors[6] I_A and I_B were determined by least-squares fit.[9]

Rate Constants.—In Table I is given a summary of the observed rate constants from absorbance measurements in unit ionic strength. Each value in the table is the result from at least two runs at 326 mμ and two

---

(5) (a) R. A. Reinhardt, *Inorg. Chem.*, **1**, 839 (1962); (b) R. A. Reinhardt, N. L. Brenner, and R. K. Sparkes, *ibid.*, **6**, 254 (1967).

(6) Supplementary material (specific kinetic data) has been deposited as Document No. 9608 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting \$3.75 for photoprints, or \$2.00 for 35-mm microfilm. Advance payment is required. Make checks payable to: Chief, Photoduplication Service, Library of Congress.

(7) The symbol k' will be used for observed (pseudo-first-order) rate constants. For the derived rate constants of the two-term rate law, k_1 refers to the first-order path and k_2 to the second-order path. Subscripts A and B are used for the first and second steps in the consecutive scheme of eq 1 and subscript C for the step leading to $\mathrm{Pd(NH_3)Cl_3^-}$.

(8) D. R. Ashley and R. Hamm, *Inorg. Chem.*, **5**, 1645 (1966).

(9) Computations were carried out on a CDC 1604 digital computer.

(10) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, pp 49, 166.

(11) Since consecutive values of E were closely spaced, it was considered valid to find E', where required, by linear interpolation.

TABLE I

RATE CONSTANTS AND DERIVED RATE PARAMETERS FOR CONSECUTIVE SUBSTITUTION OF NH_3 BY Cl^- IN $Pd(NH_3)_4^{2+}$ AT $\mu = 1$

$[Cl^-]$, M	20°	25°	30°	35°
	$k_A' \times 10^3$, sec^{-1} [a]			
0.10	1.30	1.9	2.7	4.3
0.20	...	...	4.0	6.0
0.29	...	3.1	...	...
0.60	3.3	5.4	8.8	13.8
1.0	5.5	8.3	...	...
	$k_B' \times 10^3$, sec^{-1} [b]			
0.10	2.4	3.9	6.5	8.7
0.20	...	...	9.8	15.2
0.29	...	9.1	...	...
0.60	13.0	19.7	25.1	40
1.0	18	30.8	...	...
Derived Rate Parameters				
$k_{A1} \times 10^3$, sec^{-1} [a]	0.8	1.1	1.6	2.4
$k_{A2} \times 10^3$, M^{-1} sec^{-1} [b]	4.5	7.1	12.2	19.3
$k_{B1} \times 10^3$, sec^{-1} [a]	0.7	0.9	1.5	2.5
$k_{B2} \times 10^3$, M^{-1} sec^{-1} [b]	19	30	40	62

[a] ±5%. [b] ±10%.

at 355 mμ; no significant difference was found in values of k_A' determined at the two different wavelengths. Uncertainties in k_A' are estimated at 5%; those in k_B' at 10%.

Also listed in Table I are the parameters of the two-term rate law

$$k' = k_1 + k_2[Cl^-] \qquad (3)$$

Within the precision of the data, eq 3 was obeyed at each temperature. No indication of the equilibrium accumulation of an intermediate was observed; *i.e.*, there was no evidence of a negative deviation at high $[Cl^-]$. Corresponding to the rate constants k_{A1}, k_{A2}, k_{B1}, and k_{B2}, respective values of $\Delta H^{\ddagger}$ (kcal) are 13 ± 1, 18.5 ± 0.5, 16 ± 3, and 14 ± 1, and of $\Delta S^{\ddagger}$ (eu) are −27 ± 3, −7 ± 1, −15 ± 10, and −16 ± 3.

The data for other ionic strengths ($\mu = [Cl^-]$) are given in Table II. The second-order constants were computed for each chloride ion concentration from eq 3, assuming k_{A1} and k_{B1} to be independent of μ and so equal to the values in Table I. The dependence on ionic strength, as shown in the last two columns of Table II, is that predicted by the Davies[12] relation, save that the small linear term in μ is apparently lacking. This may be attributed in part to the considerable range in salt concentration and to the fact that the effective ionic radius for Pd(II) complexes may be considerably different from those of the average ions originally chosen by Davies for his treatment. Values extrapolated to infinite dilution are $k_{A2}^0 = 0.06$ M^{-1} sec^{-1} and $k_{B2}^0 = 0.11$ M^{-1} sec^{-1} at 25°. It should be noted that for both steps k_2^0 is larger by an order of magnitude than the values found at $\mu = 1$. It is also gratifying that values of k_{A2} derived from pH measurements agree with those from absorbance measurements.

TABLE II

RATE CONSTANTS AT 25° AND $\mu = [Cl^-]$

$[Cl^-]$, M	$k_A' \times 10^3$, sec^{-1}	$k_B' \times 10^3$, sec^{-1}	$(\text{Log } k_{A2}) + [2\mu^{1/2}/(1+\mu)^{1/2}]$	$(\text{Log } k_{B2}) + [\mu^{1/2}/(1+\mu)^{1/2}]$
0.056[b]	2.38	...	−1.25	...
0.10[a]	3.33	8.00	−1.17	−0.91
0.10[b]	3.07	...	−1.23	...
0.19[b]	3.92	...	−1.22	...
0.24[b]	4.22	...	−1.23	...
0.30[a]	4.80	15.2	−1.21	−0.97
0.46[b]	5.45	...	−1.22	...
0.60[a]	6.80	22.5	−1.15	−1.00
0.92[b]	7.67	...	−1.19	...
1.0[a]	8.3	30.8	−1.14	−1.02

[a] From absorbance measurements. [b] From pH measurements.

A careful examination of the data shows no evidence of dependence of the rates on $[H^+]$. One example is seen in the agreement of absorbance with pH measurements, even though $[H^+]$ was larger by a factor of 10 in the former. A second is seen from a comparison of the following pH runs, both at 0.24 M Cl^- and 0.70 mM Pd: for $[H^+]_\infty = 0.9$ mM, $k_A' = 0.00411$ sec^{-1}; for $[H^+]_\infty = 4.4$ mM, $k_A' = 0.00429$ sec^{-1}.

Formation of $Pd(NH_3)Cl_3^-$.—After the formation of $Pd(NH_3)_2Cl_2$ was substantially complete, the absorbance continued to change very slowly. The effect was noticeable at 325 and 355 mμ only at the higher temperatures, but was more marked at 290 mμ, a fact consistent with the formation of $Pd(NH_3)Cl_3^-$. A virtually linear dependence of absorbance with time was observed, which shows that $[Pd(NH_3)_2Cl_2] = [\Sigma Pd]$ during the course of the runs (2–3 hr). We have estimated $d\bar{\epsilon}/dt$ ($\bar{\epsilon}$ = observed molar extinction coefficient) in this linear region for a few runs which have served to indicate provisionally the dependence on temperature, $[Cl^-]$, and wavelength. We present these preliminary data in terms of

$$d\bar{\epsilon}/dt = (\epsilon_1 - \epsilon_2)(k_{C1} + k_{C2}[Cl^-]) \qquad (4)$$

where[7] ϵ_1 and ϵ_2 are the molar extinction coefficients of $Pd(NH_3)Cl_3^-$ and $Pd(NH_3)_2Cl_2$, respectively. We find $k_{C2}/k_{C1} = 1.4$ M^{-1}. Writing $a_{\lambda,t} = (\epsilon_1 - \epsilon_2)k_{C1}$: $a_{290,35} = 0.015$ M^{-1} cm^{-1} sec^{-1}, $a_{290,30} = 0.008$ M^{-1} cm^{-1} sec^{-1}, $a_{326}/a_{290} = 0.04$, and $a_{355}/a_{290} = -0.03$. The correction term, I_C, of eq 2 has been estimated on the basis of these data.

Although the spectrum of $Pd(NH_3)Cl_3^-$ is not known, ϵ_1 should satisfy the above and also be consistent with the following measured or estimated values of ϵ_2: ~10 at 290 mμ, 85 at 326 mμ, and 125 at 355 mμ. Assuming a band for $Pd(NH_3)Cl_3^-$ of the same height and width as that[13] of $PdCl_4^{2-}$ in this wavelength region, we roughly estimate ϵ_1 as not less than 3×10^3 at 290, 10^2 at 326, and ~0 at 355 mμ. On this basis we estimate rate constants as follows: $k_{C1} \times 10^6$ (sec^{-1}) = 5 at 35° and 3 at 30°; $k_{C2} \times 10^6$ (M^{-1} sec^{-1}) = 7 at 35° and 4 at 30°. For either path $\Delta H^{\ddagger}$ ~22 kcal and $\Delta S^{\ddagger}$ ~ −10 eu.

Discussion

The two-term rate law is seen to hold for the substitution of Cl^- for NH_3 in palladium(II) complexes,

---

(12) C. W. Davies, *Progr. Chem. Kinetics*, **1**, 163 (1961).

(13) S. C. Srivastava and L. Newman, *Inorg. Chem.*, **5**, 1506 (1966).

an observation which reinforces the conclusion of Pearson and Johnson[4] as to the generality of this behavior for d^8 complexes. Each of the consecutive steps consists of two parallel paths. The effect of ionic strength further supports the existence of the k_2 path, the direct bimolecular substitution. The k_1 path (chloride independent) is presumed, as with platinum(II) complexes,[2b] to involve substitution by water. It is now pertinent to consider the rate of anation of the resulting aquo species. From the aquation rate and equilibrium constants,[14] we compute the rate constant for the anation of $Pt(NH_3)_3(OH_2)^{2+}$ to be 9.6×10^{-3} M^{-1} $\sec^{-1}$. Combined with a minimum rate factor[3] for Pd:Pt this leads to a lower limit of 10^2 M^{-1} $\sec^{-1}$ for the anation rate constant of $Pd(NH_3)_3(OH_2)^{2+}$. This result is also in agreement with the very rapid rate of anation observed[4] for $Pd(acac)(OH_2)_2^+$. We argue, therefore, that effective equilibrium exists in the palladium(II) systems between aquated and anated species. Under the conditions of the present work, it can be shown from the known equilibrium constants[5b] that the concentration of aquated species never exceeds more than a few per cent of the total Pd.

On the basis of the foregoing we may eliminate other parallel paths which would otherwise be allowed from the kinetics alone. A step such as

$$Pd(NH_3)_3(OH_2)^{2+} + Cl^- \longrightarrow Pd(NH_3)_2(OH_2)Cl^+ + NH_3$$

cannot have a rate constant much different from k_{A2}, and thus, owing to the low concentration of $Pd(NH_3)_3(OH_2)^{2+}$, cannot contribute appreciably to the mechanism.

The order of reactivities in the chloride-dependent steps is $k_{B2} > k_{A2} > k_{C2}$. A similar order, attributed to both *cis* and *trans* effects, was observed[15] in the consecutive substitution of Cl^- in $PdCl_4^{2-}$ by ligands of greater *trans* effect than chloride. The analogous explanation may be used for the present case also, since the *trans* effect of Cl^- is greater than that of NH_3.[2a] Moreover, it may hence be asserted that $Pd(NH_3)_2Cl_2$ is formed in our experiments predominantly as the *trans* isomer. Such assignment is, of course, consistent with the reported isomeric purity of the product so prepared[16] and also with the similar behavior[17] of dinitrodiamminepalladium(II).

If it is assumed that there is no effect on rate due to the charge[18,19] on the complex, the relative *trans* effect of Cl^- *vs.* NH_3 (including a statistical factor) is $4k_{B2}/k_{A2} = 17$ at 25° and $\mu = 1$ (*ca.* 8 at $\mu = 0$) for substitution of NH_3 by Cl^-. A corresponding *trans* effect of *ca.* 2 holds for aquation[19] of the chloroammine complexes of platinum(II); the much larger effect observed by us is consistent with the large (10:1) Br^- *vs.* Cl^- effect observed in the substitution of acac by halide[4] in $Pd(acac)X_2^-$.

Similarly, the very slow reaction of *trans*-$Pd(NH_3)_2Cl_2$ with Cl^- may be ascribed to a very large *cis* deactivation by chloride ion. The quantitive *cis* effect of NH_3 *vs.* Cl^-, $(k_{A2}/2k_{C2})^{1/2}$, can at present be only estimated ($\sim$30), but it appears to be an order of magnitude greater than that found for Pt(II) complexes.[19]

In Table III are given rate constants and activity parameters for the substitution of Cl^- and H_2O by NH_3, computed from the present results combined with the thermodynamic data[5b,20] for the system. For substitution of Cl^- both *cis* (NH_3:Cl^-) and *trans* (Cl^-:NH_3) effects are *ca.* 10:1.

TABLE III
SUBSTITUTION OF X BY NH_3 IN Pd(II) COMPLEXES AT 25°[a]

	$Pd(NH_3)_3X$	$Pd(NH_3)_2XCl$[b]	$Pd(NH_3)XCl_2$[b]
	$X = Cl^-$		
k_2, M^{-1} $\sec^{-1}$	1.2×10^2	$18. \times 10^3$	~1
$\Delta H^{\ddagger}$, kcal	8	4	...
$\Delta S^{\ddagger}$, eu	−20	−30	...
	$X = H_2O$		
k_2, M^{-1} $\sec^{-1}$	10^4	10^4	$\sim10^2$ [c]

[a] Computed from results in Table I and thermodynamic data.[5b,20] [b] Assuming *trans*-$Pd(NH_3)_2Cl_2$ predominates in both kinetics and equilibrium experiments. [c] Aquation equilibrium constant for $Pd(NH_3)Cl_3^-$ estimated at 0.006.

For the substitution of NH_3 by H_2O and for the reverse process a large *cis* effect again is apparent, but the *trans* effect, if present at all, is small.

As with the platinum(II) complexes,[2c] the entropies of activation shown in Tables I and III are all negative, presumably owing to increased bonding during the course of reaction. We may also compare the enthalpies of activation of Table III with those for the substitution[21] of Cl^- by NH_3 in $PtCl_4^{2-}$ (16.6 kcal) and in $Pt(NH_3)Cl_3^- \rightarrow$ *cis*-$Pt(NH_3)_2Cl_2$ (15 kcal). The smaller values of $\Delta H^{\ddagger}$ for Pd(II) are in the direction to be expected from a greater tendency to form a five-bonded intermediate.

From the data given by Banerjea, Basolo, and Pearson[22] estimates of the second-order rate constants (in M^{-1} $\sec^{-1}$) for the substitution of Cl^- by NH_3 may be made for *trans*-$Pt(NH_3)_2Cl_2$ (0.02) and $Pt(NH_3)_3Cl^+$ (4×10^{-4}). Comparison with the values of Table III shows relative rates of Pd to Pt of 10^5 and 3×10^5, quite in accord with the relative rates for the systems studied earlier.[3]

Acknowledgment.—The authors wish to express their great appreciation to Mrs. Lucille C. Smithson for her assistance with the experimental work.

---

(14) F. Aprile and D. S. Martin, Jr., *Inorg. Chem.*, **1**, 551 (1962).

(15) L. Cattalini, A. Orio, and M. Nicolini, *J. Am. Chem. Soc.*, **88**, 5734 (1966).

(16) R. Layton, D. W. Sink, and J. R. Durig, *J. Inorg. Nucl. Chem.*, **9**, 1965 (1966).

(17) H. B. Jonassen and N. J. Cull, *J. Am. Chem. Soc.*, **73**, 274 (1951).

(18) No conclusions can be drawn from the present work as to whether charge *per se* affects the rates. That there might be such an effect is shown from an examination of the results of Martin and his co-workers,[19] from which it can be shown that the rate of anation of $Pt(NH_3)_x(OH_2)Cl_y$ increases with increasing positive charge on the complex.

(19) M. A. Tucker, C. B. Colvin, and D. S. Martin, Jr., *Inorg. Chem.*, **3**, 1373 (1964).

(20) Erratum: In the abstract of ref 5b the equilibrium constant for the substitution of NH_3 by Cl^- in $Pd(NH_3)_3Cl^+$ should read 1.6×10^{-5}.

(21) A. A. Grinberg, *Zh. Neorgan. Khim.*, **4**, 683 (1959); quoted by F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 47 (1961).

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