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Equilibria among the Chloroammine Complexes of Palladium(II)[1]

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Potentiometric and spectrophotometric studies have been made of the equilibria among several chloroammine complexes of Pd(II) in ammonium salt solutions at 25 and 30°. For unit ionic strength at 25°, equilibrium constants found potentiometrically for the substitution of one NH_3 by Cl^- are: in $Pd(NH_3)_4{}^{2+}$, 6.1×10^{-5}; $Pd(NH_3)_3Cl^+$, 1.6×10^{-4}; $Pd(NH_3)_2Cl_2$, 1.9×10^{-6}. Aquation constants are, similarly: $Pd(NH_3)_3Cl^+$, 0.0010; $Pd(NH_3)_2Cl_2$, 0.0047. $\Delta H°$ for the substitution by Cl^- of each of the first two NH_3 molecules in $Pd(NH_3)_4{}^{2+}$ is estimated as 10 kcal.

The solubility of *trans*-dichlorodiamminepalladium(II) in dilute electrolyte solutions was reported in a previous paper[2] and the effects observed were explained there on the basis of the aquation of the neutral complex. That study was limited in scope by the necessity of making corrections to infinite dilution. As a prelude to an investigation of the kinetics of the interaction of hydrochloric acid with tetraamminepalladium(II) ion, we have designed and carried out the experiments described herein, in a constant ionic medium (1 *M* ammonium salt), primarily to investigate the equilibria among $Pd(NH_3)_4{}^{2+}$, $Pd(NH_3)_3Cl^+$, and $Pd(NH_3)_2Cl_2$.[3] As a consequence, however, of the power of the potentiometric method of Bjerrum,[4] which was the basis for many of our experiments, it has also been possible to determine or estimate equilibrium constants for the formation of several other complexes of this mixed-ligand system.

Experimental Section

Equipment.—Measurements of pH were made using a Beckmann Model GS pH meter for the potentiometric titrations and a Beckmann Research Model meter for the spectrophotometric studies. Standard-size glass and calomel electrodes were used. Commercial aqueous buffer solutions were used as reference, and thus meter readings represented nominal rather than actual values of the pH for the salt solutions employed.

Spectrophotometric data were taken on a Beckmann Model DU spectrophotometer provided with thermostated cell holder. Matched fused-silica cells were used, of 1-cm path length for the runs at 25° and of 10-cm length at 30°. The reference solution was 1.0 *M* ammonium chloride.

Materials.—$Pd(NH_3)_4Cl_2 \cdot H_2O$ was prepared by adding aqueous ammonia to a solution of $PdCl_2$, dissolving the resulting $[Pd(NH_3)_4][PdCl_4]$ in excess ammonia, and crystallizing the solid by evaporation at room temperature. Solutions containing $Pd(NH_3)_4{}^{2+}$ were made either from this solid or by dissolving $Pd(NH_3)_2Cl_2$ in a calculated quantity of aqueous ammonia.

trans-$Pd(NH_3)_2Cl_2$ was prepared by the gradual addition of small increments of hydrochloric acid to a solution containing $Pd(NH_3)_4{}^{2+}$. As soon as a slight excess of acid was present, the solid was separated, washed with iced water and ethanol, and dried. Precaution was taken to avoid elevated temperatures or prolonged contact with excess acid in order to avoid the formation of acidic impurities.[5]

The analysis of Pd, using dimethylglyoxime, has been described previously.[2] Analysis was always performed on an aliquot of the solution actually used for a run.

Potentiometric Titrations.—Stock solutions of *trans*-$Pd(NH_3)_2Cl_2$ in ammonium nitrate plus ammonium chloride were prepared and aged for at least 24 hr (with the exception of a single run, which was used 6 hr after preparation). To 50.0 ml of stock solution were added increments of a solution of ammonia containing ammonium salts of identical concentration as the stock. After each addition, 10 min was allowed for the establishment of equilibrium at 25.00° and the pH was then read. Each run consisted of 15–20 points. Due allowance was made for the decrease in palladium concentration during each run.

Blanks were performed for each ammonium nitrate–ammonium chloride concentration to establish the dependence of the pH reading on the actual concentrations of hydrogen ion and ammonia. The pH was measured after each addition of a number of small increments, first of hydrochloric acid and then of ammonia, so as to cover the range of pH experienced in the actual run.

Spectrophotometric Measurements.—Each solution was prepared by adding a small quantity of hydrochloric acid or ammonia to a stock solution of $Pd(NH_3)_4{}^{2+}$ in 1 *M* ammonium chloride and was allowed to equilibrate 30–40 min at 25.00 or 30.00°. The optical absorbance at 330 $m\mu$ and the pH were then measured. A fresh solution was prepared from the stock for each determination. Acid blanks were run, similar to those described above.

Establishment of Equilibria.—Spectra of solutions of $Pd(NH_3)_4{}^{2+}$, $Pd(NH_3)_2Cl_2$, and $PdCl_4{}^{2-}$ (the latter two in 1 *M* chloride) showed maxima in absorption at 295, 380, and 475 $m\mu$, respectively, in agreement with published data.[6] At stoichiometries midway between the above, well-defined spectra were observed with maxima at 330 and 430 $m\mu$, respectively, due undoubtedly to $Pd(NH_3)_3Cl^+$ (a species proposed earlier by Jonassen and Cull[7]) and $Pd(NH_3)Cl_3{}^-$.

Using positions of absorption maxima as a guide, we have found that the formation of $Pd(NH_3)_2Cl_2$ from acidified $Pd(NH_3)_4{}^{2+}$ is substantially complete in 3 min at 25°, 1 *M* chloride. Further reaction, however, is much slower: 12–24 hr is required for the production of $Pd(NH_3)Cl_3{}^-$ and several weeks for $PdCl_4{}^{2-}$. In the spectrophotometric measurements, owing to the relatively short times allowed, equilibrium was thus established as far as $Pd(NH_3)_2Cl_2$, but not $Pd(NH_3)Cl_3{}^-$.

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

[2] R. A. Reinhardt, *Inorg. Chem.*, **1**, 839 (1962).

[3] Since the extents of the *cis–trans* equilibria are not known for the various species for which isomers exist, the corresponding formulas will be written without prefix. The designation "*trans*-$Pd(NH_3)_2Cl_2$" will be reserved for the solid.

[4] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957.

[5] A commercial sample of $Pd(NH_3)_2Cl_2$ examined by us showed a low Pd analysis and a slightly high Cl analysis. When the solid was treated with aqueous sodium chloride, the first wash took on the unmistakable orange color of the trichloro or tetrachloro complex, though succeeding washes were colorless. It is possible that $NH_4[Pd(NH_3)Cl_3]$ was present as an impurity.

[6] A. B. Babayeva and R. I. Rudyi, *Zh. Neorgan. Khim.*, **1**, 921 (1956); A. J. Cohen and N. Davidson, *J. Am. Chem. Soc.*, **73**, 1955 (1951). It seems reasonable that the absorption maximum reported by Babayeva and Rudyi as 430 $m\mu$ for aqueous ammonium tetrachloropalladate(II) indicates extensive formation of $Pd(NH_3)Cl_3{}^-$.

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

With the solutions used for the potentiometric measurements, the time of equilibration was sufficiently long to permit the formation of $Pd(NH_3)Cl_3^-$ (but not $PdCl_4^{2-}$) by disproportionation of the diammine. That this disproportion occurred was shown by the increase in absorbance at 330 and especially at 430 mμ, observed when $Pd(NH_3)_2Cl_2$ solutions were allowed to stand. A Beer's law check eliminated polymerization as a possible cause of this spectral change. When these solutions were treated with aqueous ammonia, both spectra and pH showed that reaction was complete in 2–3 min, demonstrating that equilibrium was established for each point in the potentiometric titrations.

Treatment of the Data

Notation and Conventions.—Concentrations are expressed as molarity (M), defined as moles of solute per liter of solution measured at room temperature, or millimolarity (mM). The molar concentration is represented in equations by the use of brackets around the formulas of corresponding species. Equilibrium data are presented as stoichiometric equilibrium constants (concentration quotients), and it is assumed that in each of the constant ionic media chosen they may be treated as constants. K_1, K_2, and K_3 represent the equilibrium constants for the substitution of one NH_3 by Cl^- in $Pd(NH_3)_4^{2+}$, $Pd(NH_3)_3Cl^+$, and $Pd(NH_3)_2Cl_2$, respectively. A_1 and A_2 are the (first) aquation constants of $Pd(NH_3)_3Cl^+$ and $Pd(NH_3)_2Cl_2$, and B_2, that of $Pd(NH_3)_2(H_2O)Cl^+$.

It is assumed throughout that the several *cis–trans* equilibria are established under the conditions of the experiment and thus that the constants reported are the appropriate combinations of those for the individual isomers.

The symbol μ is used for ionic strength in molar units.

Blanks.—Parameters for each blank run[8] were computed using a least-squares fit.[9] The parameters are: $K_a = [NH_3][H^+]/[NH_4^+]$; $D = [H^+](10^{pH})$, in which pH represents the meter reading; C_0, which represents a small ammonia impurity (*ca.* 10^{-5} M) in the salts. For the blanks run at $\mu = 1.0$–1.1, the average K_a found was $(4.29 \pm 0.13) \times 10^{-10}$; for the two runs at $\mu = 0.5$, $K_a = (5.11 \pm 0.13) \times 10^{-10}$. Combining Bjerrum's[4] values of K_a at 30° and these salt concentrations with the temperature coefficient found by him in 2 M salt,[10] we compute, for 25°, 4.25×10^{-10} at $\mu = 1$ and 5.35×10^{-10} at $\mu = 0.5$.

The parameter D represents the correction for the activity coefficient of hydrogen ion (relative to infinite dilution, since aqueous buffers were used as reference) for the liquid-junction potential and, presumably, for variations in the response characteristics of the glass electrode. D varied randomly from run to run without correlation with concentrations of solutes; the range was 1.05–1.25. In the computation of $\bar{n}$ described below, the value of D (and of C_0) used was obtained from the blank which most closely corresponded in history to the palladium run being computed, usually having been carried out on the same day.

Potentiometric Titrations.—Using values of the parameters K_a, D, and C_0, as described above, the ligand number for substitution of chloride by ammonia in $Pd(NH_3)_2Cl_2$ was computed for each point.[8] This ligand number is defined by

$$\bar{n} = ([H^+] - [NH_3] + [NH_3]_0)/\Sigma[Pd]$$

in which $[NH_3]_0$ represents the number of moles of ammonia added per liter of final solution, and $\Sigma[Pd]$, the total palladium concentration. It should be noted that $\bar{n}$, as used here, gives no direct information regarding the extent of aquation of any of the species. Since $Pd(NH_3)_4^{2+}$ is the ultimate product with excess ammonia, $\bar{n}$ should approach 2.0 asymptotically. We have found that the asymptote is occasionally slightly less, but more frequently somewhat greater than 2.0 (with an extreme range, over all the runs, of 1.97–2.08). This effect is due chiefly to errors in D and in the analyzed concentration of the ammonia reagent, to which the value of the asymptote is very sensitive. For the computations described below, points for which $\bar{n} \geq 2.0$ were not used in the fitting.

Figure 1 shows $\bar{n}$ *vs.* $-\log$ $[NH_3]$ for one run at 0.1 M NH_4Cl and one at 0.005 M NH_4Cl, each 1 M in NH_4NO_3. The solid lines have been computed from the equilibrium constants of Table I.

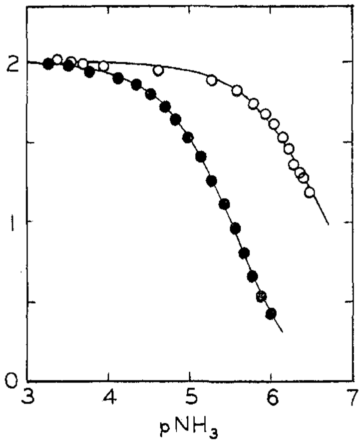

Figure 1.—$\bar{n}$ *vs.* pNH_3 for $Pd(NH_3)_2Cl_2$ in 1.00 M NH_4NO_3 at 25°: open circles, 0.005 M NH_4Cl; closed circles, 0.10 M NH_4Cl.

The data were fitted to the five equilibrium constants K_1, K_2, K_3, A_1, and A_2. B_2 was included in the computations, even though it is not well enough defined to be determined, for the value assumed for B_2 has some influence on the other constants, especially A_1 and A_2. On a purely statistical basis we have selected $B_2 = {}^1/_4A_2$. The data were almost totally insensitive to selected values of A_3, and it could be shown that the concentration of $Pd(NH_3)(H_2O)Cl_2$ never represented an appreciable fraction of the palladium content.

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[8] Detailed tables of data have been deposited as Document No. 9166 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 \$2.50 for photoprints, or \$1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[9] Computations were carried out on a CDC 1604 digital computer. The least-squares fits made use of a subroutine designed by Dr. W. M. Tolles of this department.

[10] Very nearly the same coefficient applies at infinite dilution: R. G. Bates and G. D. Pinching, *J. Res. Natl. Bur. Std.*, **42**, 419 (1949).

TABLE I

RESULTS OF POTENTIOMETRIC TITRATIONS OF $Pd(NH_3)_2Cl_2$ WITH NH_3 AT 25°

C_{NH_4Cl}	10^5K_1	10^5K_2	$10^5K_3{}^b$
1.00 *M* $NH_4NO_3{}^a$			
0.100	6.35	1.32	0.191
0.100[c]	5.11	1.82	0.091
0.100[c]	6.99	1.47	0.234
0.050	6.67	1.69	0.191
0.050	6.43	1.73	0.193
0.010	5.65	1.39	...
0.010	6.42	1.06	...
0.010[c]	4.80	1.86	...
0.010[c]	5.17	1.87	...
0.005	8.08	1.17	...
0.005	6.45	1.24	...
0.000[c]	5.83	1.64	...
0.000[c]	5.58	1.88	...
Mean value, $\mu = 1$	6.12	1.55	0.19
Std dev	0.90	0.29	0.05
0.50 *M* $NH_4NO_3{}^d$			
0.010	7.75	2.88	...
0.010	7.72	2.90	...

[a] Fitted using $A_1 = 0.0010$, $A_2 = 0.0047$, $B_2 = {}^1/_4A_2$. Uncertainties in A_1 and A_2 estimated at 25%. Initial [Pd] = 1.01 m*M*, except as noted. [b] Where not listed, K_3 was set equal to 0.19×10^{-5} for the fit. [c] Initial [Pd] = 1.98 m*M*. [d] Initial [Pd] = 0.99 m*M*. $A_1 = 0.00080$ (av), $A_2 = 0.0025$, $B_2 = {}^1/_4A_2$, assumed as described in text.

The ligand number (defined as above) is given by

$$\bar{n} = \frac{2[NH_3]^2 + E[NH_3] + C/[NH_3]}{[NH_3]^2 + E[NH_3] + G + C/[NH_3]}$$

where the conditional constants,[11] effective at constant $[Cl^-]$, are defined by

$$E = K_1(A_1 + [Cl^-])$$

$$G = K_1K_2(A_2B_2 + A_2[Cl^-] + [Cl^-]^2)$$

$$C = K_1K_2K_3[Cl^-]^3$$

Except for a few points at low $\bar{n}$, the term involving K_3 is quite negligible. The remaining constants were thus found by a fit[9] of $\bar{n}$ to $[NH_3]$ and $[Cl^-]$,[12] using the points for $1.0 \leq \bar{n} < 2.0$ from all runs at $\mu = 1$. The results of this fit are: K_1, 6.21×10^{-5}; K_2, 1.51×10^{-5}; A_1, 0.0010; A_2, 0.0047; B_2 (assumed), 0.0012.

These values of A_1, A_2, and B_2 were then used to fit each run separately at $\mu = 1$; for the runs at 0.1 and 0.05 *M* chloride, K_1, K_2, and K_3 were evaluated; for the remainder, K_3 was set at 1.9×10^{-6} and K_1 and K_2 only were found. For $\mu = 0.5$, it was assumed that K_1A_1, K_2A_2, and K_3 were independent of ionic strength (since they correspond to reactions in which there is no change of charge) and, using these quantities from the data at $\mu = 1$, K_1 and K_2 were evaluated. Results from the separate runs are given in Table I. The averages for K_1 and K_2 reported in Table I agree quite satisfactorily with the values given in the preceding paragraph. K_3 is poorly defined, and, in fact, the experiments were designed to avoid as much as possible the complications resulting from the presence of $Pd(NH_3)Cl_3^-$.

The slightly higher values of K_1 and K_2 at $\mu = 0.5$ are about what is to be expected if activity coefficients are continuing to fall with increasing ionic strength. If amido or hydroxo complexes were being formed to any appreciable extent, these equilibrium constants should be lower at lower concentrations of ammonium ion.

Spectrophotometric Data.—It can be deduced from the results of the potentiometric titrations that in 1 *M* chloride the aquo species will be present at only small concentrations; furthermore, as discussed above, $Pd(NH_3)Cl_3^-$ will not be produced in these experiments. Thus the observed absorbance is due to $Pd(NH_3)_4{}^{2+}$, $Pd(NH_3)_3Cl^+$, and $Pd(NH_3)_2Cl_2$ only. The absorbance is related to $[H^+]$ through

$$-\log (I/I_0) = \frac{L\Sigma[Pd](\epsilon_4 + \epsilon_3K_1[H^+]/K_a + \epsilon_2K_1K_2[H^+]^2/K_a{}^2)}{1 + K_1[H^+] + K_1K_2[H^+]^2}$$

in which L is the path length and ϵ_2, ϵ_3, and ϵ_4 are the molar extinction coefficients for $Pd(NH_3)_2Cl_2$, $Pd(NH_3)_3Cl^+$, and $Pd(NH_3)_4{}^{2+}$, respectively.

The concentration of hydrogen ion was computed from values of *D*, measured as described above. For K_a we have used our value of 4.29×10^{-10} at 25° and that of Bjerrum,[4] 5.9×10^{-10}, at 30°. The data[8] of each run were fitted by the least-squares program[9] to K_1, K_2, and the three extinction coefficients. For three runs at 25° we find: $10^5K_1 = 4.50, 4.83, 4.45$; $10^5K_2 = 1.78, 1.21, 1.37$. For two runs at 30°, $10^5K_1 = 5.95, 6.18$; $10^5K_2 = 1.97, 2.38$. Average values found for ϵ_2, ϵ_3, and ϵ_4, respectively are: 88, 233, and 62 at 25°; 80, 219, and 53 at 30°.

Figure 2 shows absorbance *vs.* pH for one run at 25° and one at 30°. These results for K_2 (at 25°) agree very well with those from Table I. On the other hand, K_1 is consistently rather lower than from the potentiometric titrations, indicative of an undetected systematic error. From the variations in temperature, $\Delta H_1°$ and $\Delta H_2°$ are estimated to be about 10 kcal each and $\Delta S_1°$ and $\Delta S_2°$ about 13 eu. The spectrophotometric data alone would indicate that $\Delta H_2°$ is greater than $\Delta H_1°$ by perhaps 1.5 kcal. This difference cannot be considered significant, however, in view of the disagreement in K_1 obtained from the two methods of measurement.

Discussion

The interpretation previously given[2] for the solubilities of $Pd(NH_3)_2Cl_2$ in aqueous sodium chloride, ammonium chloride, and ammonium nitrate involved the tacit assumption that only diammine species were present. It is apparent that this assumption is no longer supportable, and thus a reexamination of the solubility data is in order.

At the higher ammonium chloride concentrations used in the earlier study the limiting solubility of $Pd(NH_3)_2Cl_2$ was observed to be 0.95 m*M*. This is the sum of $[Pd(NH_3)_2Cl_2]$, $[Pd(NH_3)_3Cl^+]$, and $[Pd(NH_3)Cl_3^-]$. Using the equilibrium constants from Table I we estimate the respective concentrations as 0.55, 0.20, and 0.15 m*M*. The excess of triammine

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[11] A. Ringbom, *J. Chem. Educ.*, **35**, 282 (1958).

[12] $[Cl^-]$ was computed after each series of iterations from the current trial values of the equilibrium constants.

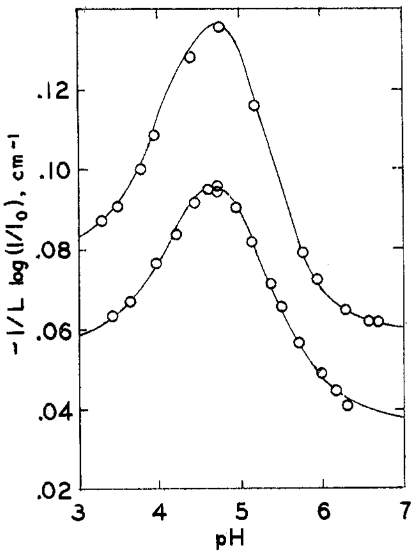

Figure 2.—Absorbance per centimeter *vs.* pH for acidified $Pd(NH_3)_4^{2+}$ in 1 *M* NH_4Cl: upper curve, 30°, 0.914 m*M* Pd; lower curve, 25°, 0.625 m*M* Pd.

over monoammine is reflected in the noticeable acidity of the solutions. We shall assume $[Pd(NH_3)_2Cl_2]$ as 0.55 m*M* in all the saturated solutions; and we estimate A_3 to be 0.006, following the general trend of A_1 and A_2. On this basis we have computed solubilities, in millimolar units, for several of the media used; experimental values are given in parentheses: 0.038 *M* NaCl, 1.03 (1.00); 0.0030 *M* NH_4Cl, 2.01 (2.00); 0.0018 *M* NH_4Cl, 2.35 (2.27); 0.0094 *M* NH_4NO_3, 2.88 (3.00); 0.094 *M* NH_4NO_3, 2.94 (3.34). The agreement is sufficient to show the consistency between the solubility data and the results of the present work, especially considering the gross approximation of using the stoichiometric equilibrium constants over such a range of ionic strength.

Benson[13] has pointed out the desirability of including a statistical correction when comparing equilibrium data for related reactions. For the substitution reaction $PdX_xY_{y-1}Z_z + Y = PdX_{x-1}Y_yZ_z + X$, the corrected constant, K^*, is given by $(y/x)K_{\text{obsd}}$. For Y = Cl, X = NH_3, values of $10^5\,K^*$ for various reactant complexes[14] are: $Pd(NH_3)_4^{2+}$, 1.5; $Pd(NH_3)_3(H_2O)^{2+}$, 2.4; $Pd(NH_3)_3Cl^+$, 1.0; $Pd(NH_3)_2Cl_2$, 0.3. The decreased tendency for $Pd(NH_3)_2Cl_2$ to undergo substitution of ammonia by chloride ion, relative to the triammine and tetraammine species, is striking (and parallels the rate effects). It is tempting to attribute the phenomenon here as due to the *cis* deactivation by Cl^-, as discussed by Tucker, Colvin, and Martin[15] for the aquation of the chloroammine species of platinum(II); for in $Pd(NH_3)_2Cl_2$, unlike the other species considered here, every NH_3, for either the *cis* or the *trans* isomer, is *cis* to a Cl^-. Substantiation of this argument, however, will require determination of the *cis–trans* equilibrium, since both isomers would have to show the effect.[16] For the reactions of the cationic complexes with Cl^-, K^* thus appears to show a decrease with decreasing positive charge, though the effect is small. Similarly, there is a slight increase for the aquation constants (K^* for $Pd(NH_3)_3Cl^+$ is 0.0010; for $Pd(NH_3)_2Cl_2$ it is 0.0024), though the effect is not as marked as that observed with the platinum complexes.[15]

For Y = H_2O, X = NH_3, the values of 10^8K^* are: $Pd(NH_3)_4^{2+}$, 1.5; $Pd(NH_3)_3Cl^+$, 2.4; $Pd(NH_3)_3(H_2O)^{2+}$, 5.8 (based on the assumed value of B_2). Comparison with such data as exist for the stabilities of platinum–ammine complexes shows that these values are of the expected magnitude. From the data of Leden and Chatt,[17] the constant for the replacement of ammonia by water in *trans*-$C_2H_4Pt(H_2O)Cl_2$ is computed to be *ca.* 10^{-8}. Grinberg and Gel'fman[18] report the cumulative instability constant of $Pt(NH_3)_4^{2+}$ (to $Pt^{2+} + 4NH_3$) as 5×10^{-36}. An extrapolation of our data leads to the estimate for $Pd(NH_3)_4^{2+}$ as 10^{-30}. It is indeed to be expected that the ligand-field stabilization of the ammine complex, relative to the aquo, will be somewhat less for Pd(II) than for Pt(II).[19]

Acknowledgments.—The assistance of Mrs. Lucille C. Smithson in carrying out some of the measurements is gratefully acknowledged. We are also indebted to the staff of the Computer Center of the Naval Postgraduate School for helpful advice.

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[13] S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

[14] It has been assumed here that the *cis–trans* isomers are distributed statistically ($^2/_3$ *cis*) and thus that all positions are equivalent. Assuming that only *trans* isomers form, respective values of 10^5K^* are: 1.5, 7.2, 3.0, 0.1.

[15] M. A. Tucker, C. B. Colvin, and D. S. Martin, Jr., *Inorg. Chem.*, **3**, 1380 (1964).

[16] The data of W. W. Dunning and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **81**, 5566 (1959), for $PtCl_2Br_2$ and those of S. C. Srivastava and L. Newman, *Inorg. Chem.*, **5**, 1506 (1966), for $PdCl_2Br_2$ are most easily interpreted on the basis of statistical isomer distribution. On the other hand, with $Pt(NH_3)(H_2O)Cl_2$ the *trans/cis* ratio[15] is 10.

[17] I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).

[18] A. A. Grinberg and M. J. Gel'fman, *Dokl. Akad. Nauk SSSR*, **137**, 87 (1961).

[19] H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).