monium 6-molybdochromate(III) as well as his refined directions for preparation of ammonium 12-molybdocerate(IV). We are also indebted to Mr. William A. Light for assistance in obtaining some of the preliminary basicity data and Mr. Donald Broadhurst for obtaining some of the coagulation data.

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Mixed Tetra-(chlorobromo)-platinates(II). Equilibrium Constants for Formation in Aqueous Solution[1]

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A radiochemical procedure, combined with a least squares treatment, has been used to obtain the four equilibrium constants for the stepwise replacement by bromide of the ligands in $[PtCl_4]^{=}$. The equilibrium constants for the single ligand replacement reactions at 25° are 14.5, 8.3, 2.0 and 1.65. The ΔH^0 for each step is estimated to be -1.8 ± 0.3 kcal. The results fail to show that the higher stability of the bromide ligand bond results primarily from π-bonding. Upper limits for the acid hydrolysis equilibrium constants in the system were also obtained.

Introduction

A radiochemical procedure has been used to evaluate the set of four equilibrium constants for the successive substitution reactions indicated by eq. 1

$$[PtCl_{4-n}Br_n]^{=} + Br^- \rightleftarrows [PtCl_{3-n}Br_{n+1}]^{=} + Cl^-, K_n \quad (1)$$

where $n = 0, 1, 2, 3$. Platinum(II) belongs to the rather limited group of ions for which the order of stability for halide ligand bonds is reversed from the normal, *i.e.*, Br^- is bonded more strongly than Cl^-.[2] Latimer[3] has estimated that for the overall reaction

$$[PtCl_4]^{=} + 4Br^- \longrightarrow [PtBr_4]^{=} + 4Cl^- \quad (2)$$

$\Delta F°$ is -6.7 kcal. In addition, Leden and Chatt[4] found an equilibrium constant of 3.4 ($\Delta F^0 = -0.72$ kcal.) for the replacement by bromide of labile chloride *trans* to ethylene in trichloro-(ethylene)-platinate(II).

The higher stability of the bromide bond, compared to chloride, may result from additional π-bonding for the bromide. Bromide has a stronger *trans*-directing effect than chloride, and Chatt, *et al.*,[5] and Orgel[6] have attributed the *trans*-directing property of a ligand to its π-bonding character.

In addition, bromide ligands in platinum(II) complexes are more labile than chloride toward exchange with the free ion.[7] Banerjea, Basolo and Pearson[8] have presented evidence that the substitutions for ligands in platinum(II) complexes are rapid for entering groups which are generally considered to provide a high degree of π-bonding. Electron pairs of the platinum ion, normally considered as non-bonding, are utilized in the π-bonds which therefore give multiple bond character for the complexes. Chatt and Wilkins[9] have found that ΔH^0 for the isomerization of *cis*- to *trans*-dichlorobis-(triethylphosphine)-platinum-(II) is nearly +2.5 kcal./mole. They suggested that the stability of the *cis*-isomer was possibly due to the π-bonding, since the two π-bonds to phosphorus could utilize both the d_{zx} and d_{zy} orbitals of platinum, whereas in the *trans*-isomer only one of these orbitals is suitable for forming π-bonds to the phosphorus atoms. Therefore, a π-bonding ligand is expected to detract from the π-bond *trans* to itself.

It appeared worthwhile to attempt an evaluation of the successive bromide substitution equilibrium constants for $[PtCl_4]^{=}$. If the stability of the platinum–bromide bond does result from its π-bond character, it is expected that $[PtCl_3Br]^{=}$ and *cis*-$[PtCl_2Br_2]^{=}$, which have no bromides *trans* to other bromides, will be especially stable. If the equilibrium constants could be determined with sufficient accuracy, it was expected that high values for K_0 and possibly K_1 would lend support to the π-bonding hypothesis.

Platinum(II) forms the well-known square complexes which are inert. Consequently, halide complexes with coördination number greater than 4 have not been considered. Ample time must be provided to attain equilibrium in the systems. At moderate halide concentration, the acid hydrolysis (or aquation) can yield the trihalide complexes according to reaction 3

$$[PtCl_{4-n}Br_n]^{=} + H_2O \rightleftarrows [PtCl_{3-n}Br_n(H_2O)]^- + Cl^-, K_{an} \quad (3)$$

where $n = 0, 1, 2, 3$.

Grantham, Elleman and Martin[10] reported 0.018 mole/l. at 25° for K_{a0}, the equilibrium constant for the aquation of $[PtCl_4]^{=}$. An evaluation of the acid hydrolysis equilibria of the mixed complexes is interdependent upon the determi-

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] B. G. F. Carleson and H. Irving, *J. Chem. Soc.*, 4390 (1954).

[3] W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 54, 59, 205.

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

[5] J. Chatt, L. A. Duncanson and L. M. Venazi, *Chemistry & Industry*, 749 (1955).

[6] L. E. Orgel, *J. Inorg. Nuclear Chem.*, **2**, 137 (1956).

[7] A. A. Grinberg and L. E. Nikolskaga, *Zhur. Priklad. Khim.*, **22**, 542 (1949).

[8] D. Banerjea, F. Basolo and R. G. Pearson, THIS JOURNAL, **79**, 4055 (1957).

[9] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 4300 (1952).

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

nation of the bromide substitution constants, the K_n's.

The Radiochemical Procedure.—To our knowledge, the experimental method for the determination of the equilibrium constants has not been utilized previously, and it deserves some comment. A weighed quantity of $K_2[PtCl_4]$ and measured volumes of standard KCl and $NaClO_4$, to adjust the ionic strength, were mixed in a volumetric flask and a small portion of Cl^{36} tracer solution was added. Water was added to bring the solution to the mark. The solution was allowed to stand for a sufficient time so isotopic equilibrium between all the exchangeable chemical forms of chlorine was assured. The chlorine of perchlorate does not exchange. A measured volume of a standard NaBr or KBr solution was added to one portion of this solution. These bromide-containing solutions remained in a thermostat for at least 40 hr. so equilibrium was again established. Aliquots were withdrawn from both the bromide-free and the bromide-equilibrated solutions. To each aliquot was added tetraammineplatinum(II) nitrate solution. $[Pt(NH_3)_4]^{++}$ precipitates the very insoluble $[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][PtBr_4]$. Grantham, *et al.*,[10] found that it also precipitated $[PtCl_3(H_2O)]^-$, apparently without fractionation from $[PtCl_4]^=$. It was therefore assumed that it precipitated effectively all the mixed anion species indicated in equations 1 and 3. The average specific activities (cts./min. g. ppt.) of the precipitates from the bromide-containing solution, $\bar{S}_i$, and from the bromide-free solution, $\bar{S}_i^0$, were determined. The ratio, $\bar{S}_i/\bar{S}_i^0$, is a measure of the extent to which complexed chloride has been replaced by bromide; and this ratio was determined for a series of bromide–chloride ratios. Since the Cl^- contents of $[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][PtCl_3(H_2O)]_2$ are virtually identical (6.662 and 6.647 mmoles/g., respectively), the aquation does not significantly influence the determination of specific activity per g. atom of chlorine in the bromide-free precipitates. However, acid hydrolysis in the bromide-containing systems must be considered. Therefore, the extent of hydrolysis was measured at four different bromide–chloride ratios.

This method possesses the advantage that necessarily laborious and difficult analyses for the individual halides in the mixtures are not required. The specific activity of the precipitates can be readily obtained by conventional radiochemical procedures, which must, however, be carefully executed. A complete recovery of precipitates need not be effected so long as a fractionation of the various complexed forms of chloride does not occur during the precipitation. The precipitates must be washed free of the solution and dried sufficiently to give representative deposits of all the chlorocomplexes.

With the consideration of acid hydrolysis in the system, a satisfying evaluation of the equilibrium constants from the data would not have been feasible without a capable electronic digital computer. An International Business Machines 650 computer was used for the calculations. With the computer it was possible to employ a least squares treatment which fully utilized the experimental data.

Experimental

Materials and Equipment.—The $K_2[PtCl_4]$ was similar to the material used by Grantham, *et al.*[10] An activation analysis of the platinum indicated an iridium impurity of *ca.* 20 μg. Ir/g. Pt.

$[Pt(NH_3)_4]Cl_2$ was prepared by the method of Keller.[11] A solution of $[Pt(NH_3)_4](NO_3)_2$ was prepared by adding $AgNO_3$ to a solution of the chloride salt. The nitrate was used as the precipitating agent for the halide complexes, so that large quantities of inactive chloride which might disturb the isotopic equilibrium would not be added. However, a small amount of chloride was allowed to remain in the solution since silver ions also precipitate the anions.

Standard solutions of KBr and NaBr were prepared by weighing the dried reagent grade salt into a volumetric flask and adding water to the mark.

Standard solutions of $NaClO_4$ were prepared by titrating NaOH with reagent grade $HClO_4$ to a *p*H of 7. The Cl^{36} tracer was obtained from the Isotopes Division of the U.S.-A.E.C., Oak Ridge, Tennessee, and it was carried in dilute HCl.

Distilled water, redistilled from alkaline $KMnO_4$, was used for the preparation of the solutions.

The counting equipment and the procedures for preparing the precipitates, for weighing and counting the samples have been described in ref. 10.

Data.—Sixteen equilibrium solutions with the tracer were prepared at 25°. All solutions contained a quantity of the $K_2[PtCl_4]$ to give a platinum concentration of 0.0166 molar. The minimum halide concentration was 0.134 molar to suppress the acid hydrolysis of the complex; however, for a chloride system the aquation amounts to 12.5%. The ionic strength was maintained at 0.318 *M* (based on zero acid hydrolysis) by the addition of the calculated amount of the standard $NaClO_4$ solution.

For each specific activity determination, five to seven samples were withdrawn and precipitated separately. The experimental conditions and results of these determinations are given in Table I. Each of the indicated uncertainties represents the standard deviation for the average, $\bar{S}_i$ or $\bar{S}_i^0$ of the *N* determinations, calculated by the expression

$$\sigma\bar{S}_i = \sqrt{\sum_i (S_i - \bar{S}_i)^2/N(N - 1)} \qquad (4)$$

The ratio of the specific activities for each solution, $R_{i-\text{obsd.}} = \bar{S}_i/\bar{S}_i^0$, is included in Table I. Its standard deviation, σR_i, was calculated by the expression

$$\sigma^2 R_i = \sigma^2\bar{S}_i/(\bar{S}_i^0)^2 + \sigma\bar{S}_i^0\bar{S}_i^2/(\bar{S}_i^0)^4 \qquad (5)$$

Five solutions were prepared which contained 0.0166 mole $K_2[PtCl_4]$/l. and different concentrations of KBr. Enough $NaClO_4$ had been added to give an ionic strength of 0.318 *M*. After equilibration with respect to aquation, the acid content was determined by rapid titration with NaOH, employing a glass electrode. A *p*H of 9 was taken as the end-point for the titrations. The equivalents of acid in the solution were assumed to equal the moles of H_2O in the trihaloaquoplatinate(II) species. Halide concentrations were purposely held to a low level so a high degree of acid hydrolysis would be provided for the experiments. The conditions and the results of these determinations appear in Table II.

Computation of Equilibrium Constants

In all of the solutions, the ionic strength was substantially constant so the activity coefficients were therefore assumed to be constant also. It is expected, therefore, that the equilibrium concentration ratios, defined in equations 6 and 7 will not vary, and they have been treated as equilibrium constants.

$$K_n = \frac{[PtCl_{3-n}Br_{n+1}^=]}{[PtCl_{4-n}Br_n^=]A} \qquad (6)$$

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(11) R. M. Keller. "Inorganic Syntheses," Vol. II. W. C. Fernelius. Ed., McGraw-Hill Book Co., Inc., New York. N. Y., 1946, p. 250.

TABLE I

EXPERIMENTAL CONDITIONS AND RESULTS FOR THE PRECIPITATION OF $[Pt(NH_3)_4][PtX_4]$–$[Pt(NH_3)_4][PtX_3(H_2O)]_2$ FROM MIXED BROMIDE–CHLORIDE SOLUTIONS

Temp. = 25°, $K_2[PtCl_4]$ added = 0.0166 mole/l., and ionic strength = 0.318 mole/l.

Cl^- added,[a] moles/l.	Br^- added, $[Br_{tot}]$, moles/l.	Specific activity of ppt., ct./min. mg. Bromide S_i	Chloride only $\bar{S}_i^0$	Obsd. ratio R_i – obsd.	Calcd. ratio R_i – calcd.	δ_i	Cl^- calcd., moles/l.	A calcd. $[Br^-]/[Cl^-]$
0.134	0.0083	47.27 ± 0.21	53.06 ± 0.30	0.891 ± 0.006	0.897	+0.006	0.1410	0.0216
.134	.0166	62.90 ± .11	77.84 ± .55	.808 ± .006	.806	– .003	.1457	.0443
.134	.0249	51.37 ± .25	69.67 ± .41	.737 ± .006	.726	– .011	.1500	.0684
.134	.0332	45.26 ± .26	68.41 ± .17	.662 ± .004	.657	– .005	.1539	.0944
.134	.0415	32.82 ± .24	55.44 ± .33	.592 ± .006	.598	+ .006	.1574	.1214
.134	.0498	31.05 ± .20	57.55 ± .36	.540 ± .005	.546	+ .007	.1605	.1500
.134	.0581	26.43 ± .20	53.37 ± .30	.495 ± .005	.499	+ .004	.1634	.1812
.134	.0664	22.56 ± .16	49.35 ± .14	.457 ± .003	.459	+ .002	.1660	.2127
.134	.0830	21.94 ± .04	54.56 ± .61	.402 ± .005	.393	– .009	.1704	.2776
.134	.0996	22.61 ± .12	66.12 ± .23	.342 ± .002	.340	– .002	.1740	.3465
.134	.1162	18.39 ± .06	63.28 ± .18	.291 ± .001	.298	+ .007	.1770	.4159
.134	.1328	16.51 ± .05	64.68 ± .40	.255 ± .002	.263	+ .007	.1796	.4881
.1188	.1494	13.94 ± .11	60.36 ± .77	.231 ± .004	.220	– .011	.1675	.6030
.1022	.1660	13.04 ± .07	68.39 ± .47	.191 ± .002	.181	– .009	.1539	.7453
.0856	.1826	12.32 ± .04	83.80 ± .56	.147 ± .001	.148	+ .001	.1398	.9202
.0690	.1992	10.97 ± .04	91.95 ± .56	.119 ± .001	.120	+ .001	.1254	1.1395

[a] In addition to 0.0664 mole Cl^-/l. in the 0.0166 mole $K_2[PtCl_4]$/l.

TABLE II

EXPERIMENTAL CONDITIONS AND RESULTS FOR THE *p*H TITRATIONS OF BROMIDE-CONTAINING SOLUTIONS OF $K_2[PtCl_4]$

Temp. = 25°, $K_2[PtCl_4]$ = 0.0166 mole/l., ionic strength = 0.318 mole/l.

Br^- added $[Br_{tot}]$, moles/l.	$[Titer_{obsd.}]$, equiv. acid/l.	$[Titer_{calcd.}]$, equiv. acid/l.
0	0.0103	0.0104
0.0090	.00786	.00791
.0179	.00590	.00588
.0408	.00285	.00282
.0827	.00105	.00104

where n = 0, 1, 2, 3 and brackets denote concentrations

$$A = [Br^-]/[Cl^-]$$

The constants for reaction 3 are

$$K_{an} = \frac{[PtCl_{3-n}Br_n(H_2O)^-][Cl^-]}{[PtCl_{4-n}Br_n^{=}]} \quad (7)$$

where n = 0, 1, 2, 3. It can be easily shown from equations 6 and 7 that the concentration of each tetrahaloplatinate(II) species is given by the general expression

$$[PtCl_{4-n}Br_n^{=}] = [Pt_{tot}]\, k_{n-1}A^n \Big/ \left(\sum_{n=0}^{4} k_{n-1}A^n + \sum_{n=0}^{3} k_{n-1}A^nK_{an}/[Cl^-]\right) \quad (8)$$

where $[Pt_{tot}]$ = total platinum concentration (0.0166 M.). $k_{-1} = 1$; $k_0 = K_0$; $k_1 = K_0K_1$; $k_2 = K_0K_1K_2$; and $k_3 = K_0K_1K_2K_3$. The concentrations of the trichloroaquoplatinates(II) are given by

$$[PtCl_{3-n}Br_n(H_2O)^-] = [Pt_{tot}]k_{n-1}A^nK_{an}/[Cl^-] \times \left(\sum_{n=0}^{4} k_{n-1}A^n + \sum_{n=0}^{3} k_{n-1}A^nK_{an}/[Cl^-]\right) \quad (9)$$

The total chloride concentration $[Cl_{tot}]$ and the total bromide concentration $[Br_{tot}]$ are known for each of the 16 experiments in Table I. However, neither A nor $[Cl^-]$ is obtained directly from the data. The calculations always started with the assumption of values for the two sets of constants, k_n and k_{an}. For each experiment in Table I $[Cl^-]$ and A were found by a trial and error reiteration in which the concentration of each species was computed by equations 8 and 9. From a set of calculated concentrations, the complexed bromide and complexed chloride concentrations, $[Br_{comp}]$ and $[Cl_{comp}]$, were calculated by equations 10 and 11

$$[Br_{comp}] = \sum_{n=0}^{4} n[PtCl_{4-n}Br_n^{=}] + \sum_{n=0}^{3} n[PtCl_{3-n}Br_n(H_2O)^-] \quad (10)$$

$$[Cl_{comp}] = \sum_{n=0}^{4} (4-n)[PtCl_{4-n}Br_n^{=}] + \sum_{n=0}^{3} (3-n)[PtCl_{3-n}Br_n(H_2O)^-] \quad (11)$$

$[Cl^-]$ and A were varied for the experiment until the calculated $[Cl_{comp}]$ and $[Br_{comp}]$ satisfied the relations 12 and 13

$$[Cl_{tot}] = [Cl_{comp}] + [Cl^-] \quad (12)$$

and

$$[Br_{tot}] = A[Cl^-] + [Br_{comp}] \pm 0.001\ M \quad (13)$$

A calculated value of $R_{i-calcd.}$ was obtained for the experiment by the expression given as equation (14), where MW = molecular weight of the corresponding $[Pt(NH_3)_4^{++}]$ – salt, 0 refers to the solution which has no added bromide. The quantity $\delta_i = R_{i-calcd.} - R_{i-obsd.}$ was next calculated. Then $\Sigma\delta_i^2/R^2_{i-obsd.}$ was evaluated for the entire set of experiments in Table I. The equilibrium constant k_0 was then changed by some increment and with such a change in k_0, a new value of $\Sigma\delta_i^2/R^2_{i-obsd.}$ was calculated. The process was repeated until the value of k_0, within a 2% change, was found

$$R_{\text{i-calcd.}} = \frac{[\text{Cl}_{\text{comp}}]\left([\text{PtCl}_4^{=}]^0\, MW + [\text{PtCl}_3(\text{H}_2\text{O})^-]^0\, MW/2\right)}{[\text{Cl}_{\text{comp}}]^0\left(\sum\limits_{n=0}^{4}[\text{PtCl}_{4-n}\text{Br}_n^{=}]\,MW + \sum\limits_{n=0}^{3}[\text{PtCl}_{3-n}\text{Br}_n(\text{H}_2\text{O})^-]\,MW/2\right)} \quad (14)$$

which gave the minimum value of $\Sigma\delta_i^2/R^2_{\text{i-obsd.}}$ Next in turn, k_1, k_2 and k_3 were each individually varied to give the minimum value in $\Sigma\delta_i^2/R^2_{\text{i-obsd.}}$ The cycle was repeated until no changes in the k_n's were obtained. Originally, a set of k_n's was evaluated with all K_{an}'s assumed equal to zero, *i.e.*, with the assumption of no acid hydrolysis. This initial set of equilibrium constants is given in Table III.

TABLE III

CALCULATED EQUILIBRIUM CONSTANTS

n	k_n (Initial set)	K_{an} (Initial set)	k_n (Final set)	K_{an} (Final set)
0	15.7	0	14.5	0.018
1	127	0	120	.0141
2	252	0	239	.0055
3	418	0	395	.0039

This initial set of k_n's from Table III was combined with a set of assumed K_{an}'s. The consistent values of $[\text{Cl}^-]$ and A were then evaluated for each experiment mentioned in Table II. The acid content $[\text{Titer}_{\text{calcd.}}]$ for an experiment was calculated by the expression

$$[\text{Titer}_{\text{calcd.}}] = \sum_{n=0}^{3}[\text{PtCl}_{3-n}\text{Br}_n(\text{H}_2\text{O})^-] \quad (15)$$

The bromide-free experiment, of course, fixes K_{a0}. The value of K_{a1} was changed (by increments of 5%) until the best fit for the acid content of the second and third points (0.0090 M and 0.0179 M total bromide) was obtained. With this new value of K_{a1}, K_{a2} was then changed until a fit with the fourth experiment was obtained. With the new values of K_{a1} and K_{a2}, K_{a3} was changed until a fit with the fifth experiment was obtained. The cycle for the calculation of the three K_{an} constants was repeated until there was no further change in them.

With the new sets of constants, k_n's and K_{an}'s, which were then at hand, the two program cycles of computation were alternately repeated until there were no further changes in any constant. The final sets of equilibrium constants are also given in Table III. It is to be noted that the final values of the k_n's were not greatly changed by the treatment which included the acid hydrolysis.

The values of $\Sigma\delta_i^2/R^2_{\text{i-obsd.}}$ for a number of trial sets of equilibrium constants, K_n, have been listed in Table IV. The minimum value of $\Sigma\delta_i^2/R^2_{\text{i-obsd.}}$ for the final set of equilibrium constants was 6.9×10^{-3}.

This value is somewhat larger than $\Sigma\sigma^2_{R_i}/R^2_{\text{i-obsd.}}$ which was 1.3×10^{-3}. Such a result suggests that other than purely statistical errors may be contained in the R_i's. However, the number of individual determinations for each condition was not sufficiently large for completely satisfactory statistics. In addition, the indicated individual values of δ_i are not alarmingly large. From Table IV it is noted that K_0 has not been established as accurately as the other K_n's. For example, a change of 30% in K_1, K_2 or K_3 more than doubles the evaluation parameter. However, a change in ΔF_0^0 of 0.25 kcal. will also double $\Sigma\delta_i^2/R^2_{\text{i-obsd.}}$ Therefore, the uncertainties in the ΔF_0^0 for the reactions in equation 1 have been arbitrarily and rather conservatively, it is believed, set at ± 0.25 kcal.

TABLE IV

DEPENDENCE OF THE EVALUATION PARAMETER $\Sigma\delta_i^2/R^2_{\text{i-obsd.}}$ UPON THE BROMIDE SUBSTITUTION CONSTANTS, K_n's WITH THE FINAL SET OF K_{an}'s FROM TABLE III

K_0	K_1	K_2	K_3	$\Sigma\delta_i^2/R^2_{\text{i-obsd.}}$
Final set				
14.5	8.30	1.99	1.65	0.0069
16.7	8.3	1.99	1.65	0.0071
18.9	8.3	1.99	1.65	.0082
9.7	8.3	1.99	1.65	.0137
14.5	7.2	1.99	1.65	.109
14.5	10.8	1.99	1.65	.154
14.5	8.3	1.73	1.65	.0201
14.5	8.3	1.99	1.90	.0216
18.9	6.4	1.99	1.65	.0136
14.5	8.3	2.59	2.15	.1807
9.7	8.3	1.99	2.48	.1210
18.7	6.4	2.58	1.27	.01410

Discussion

For the bromide substitution reactions 1, the charges of product ions are the same as the charges of the reactant ions. Since in all the experiments the ionic strength was substantially constant, the calculated equilibrium constants, k_n or K_n, given in Table III and IV, are expected to be a very good measure of the standard free energy changes of the reactions according to the familiar expression

$$\Delta F_n^0 = -RT \log_e K_n \quad (16)$$

Values of the indicated ΔF^0 for the four successive bromide substitution reactions are given in Table V. Latimer and Jolly[12] have proposed a means to estimate ΔS^0 for the replacement of H_2O in a metal ion complex by a ligand. An extension of their method gives $\Delta S^0 = -3.3$ e.u. for the replacement of chloride by bromide on a metal ion complex in the +2 oxidation state, *i.e.*, for each of the reactions in equation 1. The entropy changes, however, must include contributions of statistical factors arising from the symmetry of the species in the reactions. The importance of such statistical factors for acid–base equilibria was

TABLE V

THERMODYNAMIC QUANTITIES AT 25° FOR THE REACTIONS

$$[\text{PtCl}_{4-n}\text{Br}]_n^{=} + \text{Br}^- \rightleftarrows [\text{PtCl}_{3-n}\text{Br}_{n+1}]^{=} + \text{Cl}^-$$

		Statistical factor			ΔH_n^0 (Estimated) kcal.		
n	ΔF_n^0, kcal.	*cis* only	*trans* only	*cis*: *trans* = 2:1	*cis* only	*trans* only	*cis*: *trans* = 2:1
0	−1.58	4	4	4	−1.74	−1.74	−1.74
1	−1.25	1	1/2	3/2	−2.23	−2.64	−1.99
2	−0.41	1	2	2/3	−1.39	−0.98	−1.63
3	−0.30	1/4	1/4	1/4	−2.10	−2.10	−2.10
	−3.54				−7.46	−7.46	−7.46

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[12] W. M. Latimer and W. L. Jolly, THIS JOURNAL, **75**, 1548 (1953).

emphasized in the review article by Brønsted[13] and the topic has recently been discussed by Benson.[14] The present experiments do not distinguish between the possible *cis*- and *trans*-isomers of dibromodichloroplatinate(II); and in the equilibrium expressions $[PtCl_2Br_2^=]$ corresponds to the sum of the two isomers' concentrations. Therefore, unambiguous statistical factors for the contribution to ΔS_1^0 and ΔS_2^0 cannot be given. The statistical factors have been included in Table V for the three cases: (1) *cis*-isomer is dominant; (2) *trans*-isomer is dominant; (3) *cis*-isomer: *trans*-isomer = 2:1. The latter case corresponds to the distribution of isomers expected on the basis of statistics alone, *i.e.*, if ΔH^0 for isomerization equals zero. The values of total entropy changes were therefore calculated from the expression

$$\Delta S_n^0 = -3.3 + R \log_e \text{ (statistical factor)} \quad (17)$$

The estimated values of $\Delta H_n^0 = \Delta F_n^0 + T\Delta S_n^0$ also included in Table V.

The high value for ΔH_2^0 together with the low value of ΔH_3^0 for the *trans*-isomer only do not appear reasonable. The alternation in values of ΔH_n^0 for the *cis*-isomer only is somewhat larger than the expected uncertainty of 0.3 kcal., and no obvious cause for such alternation is apparent. In particular, the estimated values of ΔH_0^0 and ΔH_3^0 are approximately equal, and there appears to be no exceptional stability indicated for the addition of the first bromide. It is believed likely, therefore, that the distribution of isomers is given approximately by the statistical ratio of *cis:trans* = 2:1. In this case, the estimated ΔH_n^0 for all the substitutions differ by no more than the uncertainties, and there is no indicated additional stability for placing a bromide ligand *trans* to a chloride rather than *trans* to a bromide.

Poulsen and Bjerrum[15] have pointed out that the assumptions of Latimer and Jolly,[12] which predict constant ΔS^0 values for successive substitution reactions, do not give ideal agreement with some metal ion–ammonia systems when the assumption of constant ΔH^0 for successive reactions is applied. Hence, variations in the actual ΔS^0 values provide additional uncertainties to the estimates for the ΔH^0 values in Table V. It is interesting to note that with an entropy change of -3.3 e.u., the ΔF^0 of -0.72 kcal. for the replacement of the *trans*-chloride in trichloro-(ethylene)-platinate (II)[3] corresponds to a $\Delta H^0 = -1.72$ kcal., in very good agreement with the estimated values for the reactions of equations 1. In that case, the *trans* ligand is believed to be strongly π-bonded.

With the substituted phosphines in the complexes which Chatt and Wilkins[9] studied, the π-bonding to phosphorus is expected to be much stronger than to bromide ligands. Also, a portion of the 2.4 kcal. which they obtained for ΔH^0 for the *cis* to *trans* isomerization of dichlorobis-(triethylphosphine)-platinum(II) may result from the interaction of the dipole moment of the *cis*-isomer with the solvent.

With the uncertainties in the values of the K_n's and the low values for the ΔH_n^0, it did not seem profitable to attempt the determination of the temperature dependence in the equilibrium constants.

Some recent experiments with $K_2[PtCl_4]$ solutions in this Laboratory have indicated that in dilute solutions with low halide concentration a second acid hydrolysis process occurs to a detectable degree according to equation 18

$$[PtCl_3(H_2O)]^- + H_2O \rightleftarrows [PtCl_2(H_2O)_2] + Cl^- \quad (18)$$

Such a second acid hydrolysis would be significant in the acid-content titration for the determination of K_{an} in Table II; but it would be negligible in the high halide solutions for the bromide–substitution experiments of Table I. Therefore, the values of K_{an} obtained must be considered upper limits to the actual first acid hydrolysis constants. In the treatment of the bromide-substitution experiments of Table I, the acid hydrolysis has therefore probably been overestimated. It is interesting to note that the four acid hydrolysis constants K_{a0}: K_{a1}: K_{a2}: K_{a3}, with the exception of K_{a2}, followed rather closely the ratios predicted by the statistical factors of 1:3/4:1/2:1/4 for the case of *cis:trans* = 2:1. Since the K_n values did not change substantially when the acid hydrolysis effect was introduced, the final set of equilibrium constants for reactions 1 appear to be valid. A further investigation of the second acid hydrolysis processes of $[PtCl_4]^=$ is underway.

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