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Kinetics of Replacement of the Halide Ligands of Platinum(II) Complexes. The Reaction of Chloride Ion with Bromo(diethylenetriamine)platinum(II)[1]

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A radiochemical technique combined with ion-exchange separation has provided both the rate law and an equilibrium quotient of 0.26 at 25° and $\mu = 0.318\ M$ for the reaction $\mathrm{Pt(dien)Br^+ + Cl^- \rightleftarrows Pt(dien)Cl^+ + Br^-}$. The rate law indicates that the reaction occurs partially by hydration in which an H_2O replaces the Br^- ligand and is in turn replaced by a chloride and partially by a second-order process. The technique has also permitted a direct measurement of $9.6 \times 10^{-5}\ M$ for the equilibrium quotient of the aquation reaction $\mathrm{Pt(dien)Br^+ + H_2O \rightleftarrows Pt(dien)(H_2O)^{2+} + Br^-}$.

Introduction

Diethylenetriamine (dien) serves as a tridentate ligand which occupies three of the coordination sites for the square-planar platinum(II) complexes. Basolo, Gray, and Pearson[3] noted that these complexes, with one other ligand, which is usually replaced much more rapidly than dien, are exceedingly valuable for systematizing the substitution kinetics of the square-planar complexes. Since only one ligand replacement is involved, treatment of the kinetics is generally simple since successive reactions need not be considered. It is also possible to study the replacement of different ligands from complexes which are otherwise identical. The effect of various leaving and entering groups upon the substitution kinetics can therefore be clearly demonstrated.

Gray[4] reported rates for substitution of halide ligands of the platinum(II)–diethylenetriamine complexes by a number of nucleophilic agents. In addition, Gray and Olcott[5] studied reactions of $\mathrm{Pt(dien)(H_2O)^{2+}}$ with various agents, including halides.

In earlier work from this laboratory[6] concerning the isotopic exchange between free Br^- ion and the Br ligand of $\mathrm{Pt(dien)Br^+}$, it was found that the cation quantitatively penetrated columns of anion-exchange resin whereas free bromide was effectively removed from the solutions. It appeared that if the Br^- ligand was tagged with ^{82}Br, the measurement of radioactivity in the effluent from the column would provide an accurate measure of the concentration of $\mathrm{Pt(dien)Br^+}$ in the solution. The present work involves a study undertaken to evaluate this technique for characterization of the kinetics for the replacement of the Br^- ligand by chloride since the method offered certain advantages over spectrophotometric methods utilized previously.[4]

Experimental Section

Separation Method.—For the separation of free bromide ion from solutions, a column of 40–100 mesh Amberlite IRA-400 anion-exchange resin in the nitrate form was utilized. The bed, 6–7 cm deep, was supported on a wad of glass wool in an 8-mm i.d. Pyrex tube. A second wad covered the bed so the resin would not be disturbed by the addition of the sample. Normally, 2.00-ml aliquots of the solutions were introduced into the column and the bulk of the solution was drained within 30 sec into a volumetric flask. Additional aliquots of H_2O were added and drained to wash the solution from the pores of the bed. This washing was completed in 2 min. The solution collected from the column was diluted to the mark in a volumetric flask, and a 25-ml aliquot was pipetted into a plastic vial. The vial was placed in a reproducible manner upon a 3 in. × 3 in. cylindrical scintillation crystal for counting. A multichannel analyzer was utilized, and the pulses under the γ-ray peaks at 0.554 and 0.777 Mev for the 36-hr ^{82}Br were counted to measure the Br which passed through the column as $\mathrm{Pt(dien)Br^+}$.

The procedure introduces an uncertainty of less than 30 sec to the separation time for *ca.* 95% of the sample. Generally, the times of introduction of the sample to the column were recorded. Radiochemical evaluation of the effectiveness of the separations indicated that less than 0.01% of bromide ion penetrated the column. The method appears very satisfactory for the treatment of reaction rates of less than 5% $\mathrm{min^{-1}}$, and with some loss of accuracy it can be used for rates as high as 10% $\mathrm{min^{-1}}$.

Procedure.—The ^{82}Br was prepared by irradiation of NH_4Br in the Ames Laboratory research reactor. After the short-lived activities had decayed, it was dissolved to form a stock solution. For a kinetics experiment the desired amount of the compound, [Pt(dien)Br]Br, was weighed into a flask and dissolved in about 2 ml of H_2O. A portion of the tagged NH_4Br solution was added, usually from a micropipet. The solution was allowed to stand for at least 8 hr to provide for uniform distribution of the tracer ^{82}Br between free bromide ion and the bromide ligand. Then the free bromide in the solution was exchanged by nitrate with the ion-exchange procedure described above. The effluent was added to a 50-ml volumetric flask in which the calculated amount of $NaNO_3$ was added to give the desired final ionic strength. H_2O was added almost to fill the flask which was then placed in a thermostat to attain the desired reaction temperature.

The reaction was initiated by adding the desired amount of a standard KCl solution and diluting to the mark with materials which had been stored in the thermostat. The concentration of $\mathrm{Pt(dien)Br^+}$ in the solution was followed by pipetting 2-ml aliquots from the reaction solution for the ion-exchange separation. This concentration was taken proportional to the counting rate, C_i, of the samples above background after the counting rates had all been converted to a common time to correct for decay during the counting period. At least two infinity counting samples, C_∞, were taken several hours after the start of the replacement reactions. If a 2-ml aliquot of the reaction solution was diluted to 25 ml and counted without the ion-exchange sepa-

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 2045.

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

[4] H. B. Gray, *ibid.*, **84**, 1548 (1962).

[5] H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962).

[6] J. E. Teggins and D. S. Martin, Jr., *ibid.*, **6**, 1003 (1967).

ration, a count rate, C_0, proportional to the total Pt(dien)Br$^+$ which had been added to the reaction flask was obtained. The value of this initial sample was not recognized initially and it was omitted from some of the early experiments.

Results and Discussion

Results for one experiment for the replacement of the bromide ligand upon the addition of Cl$^-$ have been shown in Figure 1. Here, two plots are shown. In the upper portion the counting rate of the samples has been plotted, and in the lower part log $[(C - C_\infty)/(C_0 - C_\infty)]$ *vs.* the time is shown. The fact, apparent from either curve, that an extrapolation of C to zero time did not yield C_0 was at first disturbing. However, it was recognized that this decrease in the counting rate might result from the reversible aquation of the complex Pt(dien)Br$^+$, according to eq 1, before the addition of Cl$^-$

$$\mathrm{Pt(dien)Br^+ + H_2O \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} Pt(dien)(H_2O)^{2+} + Br^-} \qquad (1)$$

An equilibrium quotient can be written for reaction 1

$$K_1 = [\mathrm{Pt(dien)(H_2O)^{2+}}][\mathrm{Br^-}]/[\mathrm{Pt(dien)Br^+}] \qquad (2)$$

An evaluation of K_1 appeared feasible therefore by the use of the ion-exchange separation technique. For 25° it was found that 79.5% of ^{82}Br in an equilibrium solution of a 1.8 mM [Pt(dien)Br]NO$_3$ solution passed the anion-exchange resin as the bromide complex, and a value of 80.6% was obtained for 35°. The indicated values of K_1 therefore were 9.6×10^{-5} M at 25° and 8.6×10^{-5} M at 35°, corresponding to a $\Delta H°$ of -2 ± 2 kcal. The reaction even at 25° approached equilibrium with a half-time of <10 min, too rapidly for a good evaluation of the rate constants. The values of K_1 were too small for as accurate an evaluation by the titration techniques utilized for other platinum(II) complexes.[7]

A value of 1.3×10^{-4} sec^{-1} was obtained for k_1[6] from the first-order term in the rate of exchange between Br$^-$ and Pt(dien)Br$^+$, in excellent agreement with the value from the replacement rate of the bromide ligand by hydroxide observed by Gray.[4] Gray and Olcott[5] reported a value of 7.0 M^{-1} sec^{-1} for k_{-1}. Since $K_1 = k_1/k_{-1}$, their result, combined with the value of 1.3×10^{-4} sec^{-1} for k_1, yields a value of 1.9×10^{-5} for the equilibrium quotient, K_1, in contrast to our value of 9.6×10^{-5} M. However, the two determinations were made at widely different ionic strengths. The ionic strength varied up to a maximum of 5.2×10^{-3} M in the experiments of Gray and Olcott; in the present work it was constant and amounted to 0.318 M. The equilibrium constant for reaction 1 can properly be written

$$e^{-\Delta F°/RT} = \frac{[\mathrm{Pt(dien)(OH_2)^{2+}}][\mathrm{Br^-}]\gamma_2\gamma_{\mathrm{Br}}}{[\mathrm{Pt(dien)Br^+}]\gamma_1\gamma_{\mathrm{H_2O}}} \qquad (3)$$

where the brackets represent molar concentration, γ_2 is the activity coefficient of Pt(dien)(OH$_2$)$^{2+}$, γ_1 is the activity coefficient of Pt(dien)Br$^+$, γ_{Br} is the activity coefficient of Br$^-$, and $\gamma_{\mathrm{H_2O}}$ is the activity coefficient of H$_2$O.

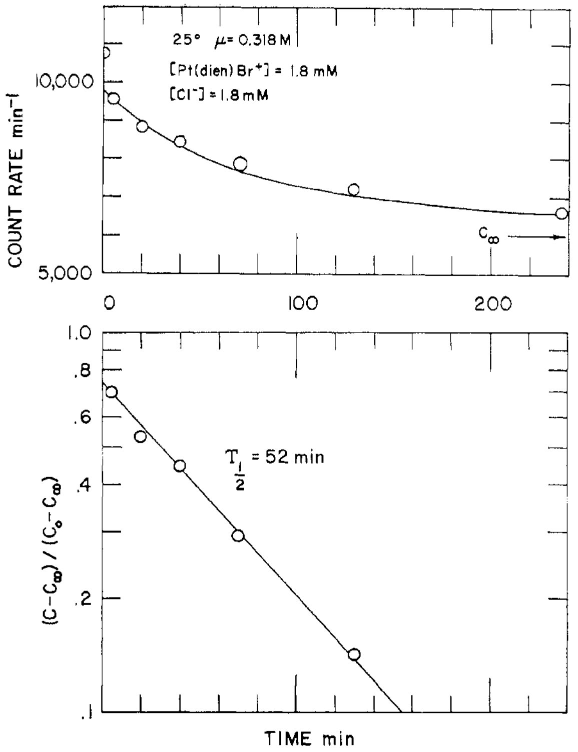

Figure 1.—The counting rate of ^{82}Br$^-$ which penetrated the ion-exchange bed as Pt(dien)Br$^+$ *vs.* time.

γ_{Br} and γ_1 are for singly charged ions so they are expected to behave similarly with ionic strength. Also $\gamma_{\mathrm{H_2O}}$ is not expected to undergo large changes. A ratio $\gamma_2(\mu = 0.318)/\gamma_2(\mu = 0.005) = 0.29$ can be estimated.[8] This ratio appears to account rather satisfactorily for the difference between the two determinations in view of the uncertainties inherent in both methods.

From Figure 1 it is clear that the replacement of the bromide is not complete, but the system approached an equilibrium state with respect to

$$\mathrm{Pt(dien)Br^+ + Cl^- \underset{R_{Cl}}{\overset{R_{Br}}{\rightleftharpoons}} Pt(dien)Cl^+ + Br^-}, \quad K_{\mathrm{Cl}} \qquad (4)$$

From the kinetics experiments in which both C_∞ and C_0 were evaluated it was possible to calculate the equilibrium quotient, K_{Cl}. First, the amount of Pt(dien)(OH$_2$)$^{2+}$ formed during the equilibration with ^{82}Br$^-$ was calculated from the equilibration conditions and K_1. In all of the experiments the zero-time concentration, $[\mathrm{Pt(dien)(OH_2)^{2+}}]_0$, was less than 0.2% of the total platinum concentration $[\mathrm{Pt}]_{\mathrm{tot}}$. However, a quantity of bromide corresponding to $[\mathrm{Pt(dien)(OH_2)^{2+}}]_0$ was removed from the solution in the initial ion-exchange replacement of the bromide.

The equilibrium concentrations are given by the equations

$$[\mathrm{Pt(dien)Br^+}]_\infty = (C_\infty/C_0)[\mathrm{Pt(dien)Br}]_0 \qquad (5)$$

$$[\mathrm{Br^-}]_\infty = [\mathrm{Pt(dien)Br^+}]_0 - [\mathrm{Pt(dien)Br^+}]_\infty \qquad (6)$$

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[7] L. F. Grantham, T. S. Elleman, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **77**, 2965 (1955).

[8] C. E. Crouthamel and D. S. Martin, Jr., *ibid.*, **73**, 570 (1951).

TABLE I

KINETICS AND EQUILIBRIUM DATA FOR THE REPLACEMENT OF THE BROMIDE LIGAND OF $Pt(dien)Br^+$ BY CHLORIDE[a]

Initial $[Pt(dien)Br^+]$, mM	Initial $[Cl^-]$, mM	$[Pt(dien)Br^+]_\infty/[Pt(dien)Br^+]_0$, C_∞/C_0[b]	Calcd $[Pt(dien)(OH_2)^{2+}]_0$, mM	Calcd $[Pt(dien)(OH_2)^{2+}]_\infty$, m$M$	Equil quotient, K_{Cl}	Half-time, min	$10^4(R_{Cl})_0$, mM/sec
25°							
0.4	180	0.0093	0.0006	0.0009	0.237	46	1.00
1.8	1.8	0.614	0.003	0.151	0.273	52	1.54
1.8	30	(0.165)				66	2.63
1.8	100	(0.0683)				54	3.58
1.8	180	0.360	0.003	0.0035	0.260	45	4.46
1.8	250	(0.0264)				39	5.20
1.8	316	0.022	0.003	0.0021	0.249	34	5.97
5.0	180	0.0919	0.008	0.0096	0.256	40	13.1
15.0	180	0.208	0.025	0.0025	0.268	37	37.0
					Av 0.26		
35°							
0.4	180	0.0092	0.0006	0.0009	0.238	16	2.87
1.8	1.8	0.594	0.003	0.138	0.340	20	4.23
1.8	30.0	0.152	0.003	0.027	0.292	23	7.65
1.8	100	0.0543	0.003	0.0055	0.302	19	10.3
1.8	180	0.349	0.003	0.0034	0.270	16	12.5
1.8	250	0.0250	0.003	0.0024	0.270	13	15.6
1.8	316	0.0196	0.003	0.0019	0.281	12	16.9
5.0	180	0.0825	0.008	0.0085	0.290	15	35.3
15.0	180	0.1975	0.025	0.0236	0.289	12.5	111
					Av 0.29		

[a] Ionic strength adjusted to 0.318 M by addition of $NaNO_3$. [b] Values in parentheses were calculated from the values of the equilibrium quotient, K_{Cl}.

With values of $[Br^-]_\infty$ and $[Pt(dien)Br^+]_\infty$ the value of $[Pt(dien)(OH_2)^{2+}]_\infty$ was next calculated from K_1. Then $[Pt(dien)Cl^+]_\infty$ was calculated from

$$[Pt(dien)Cl^+]_\infty = [Pt]_{tot} - [Pt(dien)Br^+]_\infty - [Pt(dien)H_2O^{2+}]_\infty \quad (7)$$

Also

$$[Cl^-]_\infty = [Cl^-]_0 - [Pt(dien)Cl^+]_\infty \quad (8)$$

The equilibrium concentrations of all four species in reaction 4 were therefore established, and from these the equilibrium quotient, K_{Cl}, for the experiment was calculated. The conditions and results for each of the kinetics experiments have been listed in Table I, where the indicated values of the equilibrium quotients have also been tabulated. The consistency of these values over a rather wide range of the concentration variables attests to the suitability of the technique. A value of 0.26 at 25° and 0.29 at 35° is consistent with the usual assignment of Pt^{II} as a "B" class ion[9] or a "soft" acid.[10] However, $\Delta H° \approx 2 \pm 2$ kcal is not large. The value $\Delta S° \approx 4$ cal/deg is close to the prediction of +3 cal/deg which can be made by the simple method of Latimer and Jolly.[11]

The present technique provides a measure of the concentration of $Pt(dien)Br^+$ as a function of time. Since reaction 4 was reversible, an initial-slope technique was utilized to find $(R_{Cl})_0$ which was the rate, $[d[Pt(dien)Br^+]/dt]_0$, for the condition that $[Pt(dien)Cl^+]_0 = 0$. Since linear plots were obtained for log $[(C - C_\infty)/(C - C_\infty)]$ *vs.* time, the evaluation of these rates from the slope (or half-time) of these logarithmic plots was considered the most judicious method. Since

$$\ln [(C - C_\infty)/(C_0 - C_\infty)] = \ln \{([Pt(dien)Br^+] - [Pt(dien)Br^+]_\infty)/([Pt(dien)Br^+]_0 - [Pt(dien)Br^+]_\infty)\} \quad (9)$$

differentiation yields

$$\frac{d \ln (C - C_\infty)}{dt} = d \ln ([Pt(dien)Br^-] - [Pt(dien)Br^+]_\infty)/dt = \frac{d[Pt(dien)Br^+]/dt}{[Pt(dien)Br^+] - [Pt(dien)Br^+]_\infty} \quad (10)$$

The value of $(-\ln 2)/\tau_{1/2}$ was taken from the linear logarithmic plots for d ln $(C - C_\infty)/dt$ and therefore the initial rates were evaluated by the expression

$$(R_{Cl})_0 = -(d[Pt(dien)Br^+]/dt)_0 = (\ln 2)([Pt(dien)Br^+]_0 - [Pt(dien)Br^+]_\infty)/\tau_{1/2} \quad (11)$$

For eq 11 $[Pt(dien)Br^+]_\infty$ was taken as $(C_\infty/C_0)[Pt(dien)Br^+]_0$ if C_0 was evaluated; for the cases in which C_0 was not evaluated it was calculated from $[Cl]_0$ and K_{Cl}. The observed half-time for each experiment is included in Table I and in the final column the indicated value of $(R_{Cl})_0$ has been listed.

The function $(R_{Cl})_0/[Pt(dien)Br^+]_0$ has been plotted *vs.* $[Cl^-]$ in Figure 2. It appears that at high chloride concentration this quantity is described very satisfactorily by straight-line functions. The second-order rate constant for k_{Cl} for reaction 4 is taken as the slope of the straight line whose intercept corresponds to the first-order constant, k_1, for reaction 1. At chloride concentrations of 30 mM and less, there is a significant deviation of the observed rate function from the straight lines. The straight-line relation requires that

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[9] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

[10] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

[11] W. M. Latimer and W. J. Jolly, *ibid.*, **75**, 1548 (1953).

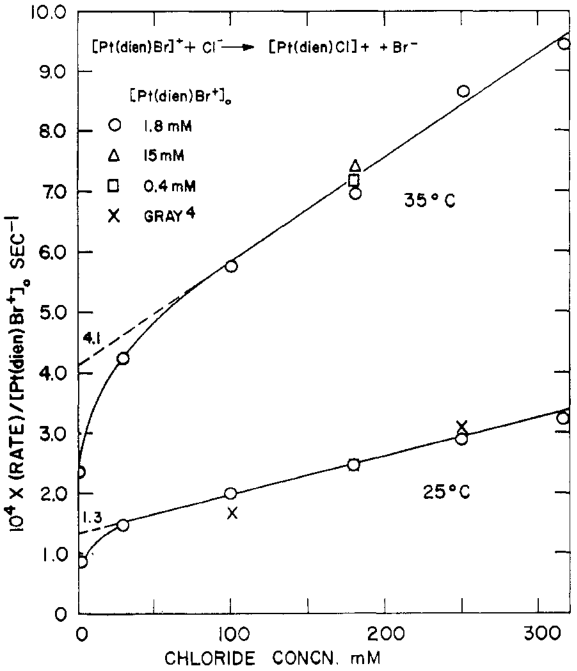

Figure 2.—Dependence of the rate of bromide replacement from Pt(dien)Br$^+$ upon the chloride concentration; ionic strength = 0.318 M.

the [Cl$^-$] be sufficiently high that it reacts to replace the water in effectively all of the Pt(dien)(OH$_2$)$^+$. Since some aquation according to reaction 1 occurred before the addition of Cl$^-$, at low Cl$^-$ concentrations the Br$^-$ ion released competed with Cl$^-$ to re-form the bromo complex. A reduction in the rate of disappearance of Pt(dien)Br$^+$ was the consequence. This effect was more pronounced at the higher temperature where the aquation was more extensive upon the addition of chloride because of its higher rate. The somewhat greater scatter of points at 35° occurred because a number of half-times were below 15 min and reflected the uncertainty in the time of separation. A second-order rate constant k_{Br} for the reverse of reaction 4 can be evaluated from the requirement $k_{\mathrm{Cl}}/k_{\mathrm{Br}} = K_{\mathrm{Cl}}$. The values of the rate constants and the activation parameters are included in Table II.

Table II

Rate Constants for Halide Replacement of the [Pt(dien)X]$^+$ Complexes at Ionic Strength = 0.318 M

Reaction	Rate constant × 10^4 25°	35°	$\Delta H^\ddagger$, kcal	$\Delta S^\ddagger$, cal/deg
Pt(dien)Br$^+$ + H$_2$O	1.3^a	4.1^a	20	−13
Pt(dien)Br$^+$ + Cl$^-$	6.0^b	17^b	18	−11
Pt(dien)Cl$^+$ + Br$^-$	23.0^b	59^b	17	−15

[a] Units: sec^{-1}. [b] Units: sec^{-1} M^{-1}.

The two points reported by Gray for reaction 4 for 25° and μ = 0.25 are shown in Figure 2. These points do not disagree seriously with the present results. However, the line drawn through these two points gives a considerably higher k_{Cl} and a lower value of k_1. The value of k_1 at 25° from the present work is confirmed by our bromide exchange[6] and Gray's[4] value from the replacement by hydroxide.

Belluco, *et al.*,[12] have characterized the reactivities of entering groups in platinum(II) complexes in terms of n_{Pt}, a nucleophilic reactivities constant. This quantity is the ratio k_2/k_s, where k_2 is the second-order constant and k_s is the first-order constant (describing the rate of solvation) for the substitution of a chloride ligand in *trans*-Pt(py)$_2$Cl$_2$ in methanol at 30°. In systematizations with this parameter, especially in aqueous solutions, it appears advisable to include ionic strength effects. This has been emphasized by Chan's recent report[13] about a series of careful experiments which indicate a strong ionic strength effect upon k_2 for the replacement of chloride and bromide ligands in Pt(dien)X$^+$ by iodide. For consideration of ionic strength effects a rate constant[14] for a reaction between the reactants, A, B, . . . , may be expressed as

$$k = k^0(\gamma_A\gamma_B\ldots/\gamma_\pm) = k^0\Gamma(\mu) \qquad (12)$$

where μ is the ionic strength, γ_A is the activity coefficient of reactant A, etc., $\gamma_\pm$ is the activity coefficient of the reactive intermediate, and k^0 is the rate constant at zero ionic strength. According to this treatment a rate constant for a reaction between two species, one of which is uncharged, will be independent of ionic strength as was the case for the reference compound in establishing n_{Pt}. It will also be expected for the solvation of a charged Pt$^{\mathrm{II}}$ complex, characterized by k_1, and such behavior has been noted.[15] At low ionic strength the function $\Gamma(\mu)$ for a reaction between Pt(dien)X$^+$ and an anion is expected at 25° to follow the function

$$\log \Gamma = -1.018\sqrt{\mu} \qquad (13)$$

Chan, in plotting log k_2 *vs.* $\sqrt{\mu}$ for the region of $0.17 < \sqrt{\mu} < 0.32$ M, obtained a linear plot with a slope -1.05 $M^{-1/2}$. To the extent that the variation in log $\gamma_\pm{}^2$ for a 1-1 electrolyte over this ionic strength region corresponds to a slope of about 0.7,[16] this result indicates a deviation of $\Gamma(\mu)$ from expected behavior. Therefore, rather than to attempt a further refinement, Chan's expression for $\Gamma(\mu)$ was used to convert the present rate constants to zero ionic strength although it is recognized that this does correspond to a dangerous extrapolation of their linear function in both directions from the measured region. For μ = 0.318, Γ amounts to the relatively small factor of 0.26. The second-order rate constants corrected in this way to zero ionic strength for halide replacement by halides in the dien complexes are collected in Table III. Gray[4] reported rates for the replacement of chloride by bromide from Pt(dien)Cl$^+$. When his rates were plotted against [Br$^-$]Γ, the indicated second-order rate constant for

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(12) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

(13) C. S. Chan, *J. Chem. Soc.*, *Sect. A*, 1000 (1966).

(14) A. A. Frost and R. G. Pearson, "Kinetics and Mehanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p 138.

(15) (a) J. E. Teggins, D. R. Gano, M. A. Tucker, and D. S. Martin, Jr., *Inorg. Chem.*, **6**, 69 (1967); (b) F. Aprile and D. S. Martin, Jr., *ibid.*, **1**, 551 (1962).

(16) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, tables on pp 716, 731–732.

TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE REPLACEMENT OF HALIDE LIGANDS OF $Pt(dien)X^+$ BY HALIDE AT 25° AND CONVERTED TO IONIC STRENGTH = 0

	Entering group		
	Cl^-	Br^-	I^-
Leaving group	10^4k_2, sec^{-1} M^{-1}		
Cl^-	150[a]	89 78[a]	3200[b]
Br^-	23	228[c]	4200[b]

[a] Reference 4. [b] Reference 13. [c] Reference 6.

zero ionic strength was 78 sec^{-1} M^{-1} which is in satisfying agreement with our value of 89 sec^{-1} M^{-1}.

The plot of log k_2 *vs.* n_{Pt} in Figure 3 for the zero ionic strength conditions is generally consistent with the expected linear behavior. Without the correction to zero ionic strength there was a much greater scatter for the points. The rate constant for the reaction of Cl^- with $Pt(dien)Cl^+$ appears the only inconsistency in the set. This rate was determined by $^{36}Cl^-$ exchange in which a silver chloride precipitation was used for the separation process.[4] Silver halide separations have proven unsatisfactory for the exchange studies of a number of platinum(II) complexes in this laboratory. It would therefore seem advisable to reexamine that system with an ion-exchange procedure.

It appears that bromide is only a slightly better leaving group than chloride for these complexes in which differences such as ionic charge and differences in the *cis* and *trans* neighbors have been eliminated. Perhaps the most striking feature which is emerging for these reactions is that chloride and bromide behave so similarly as a leaving group.

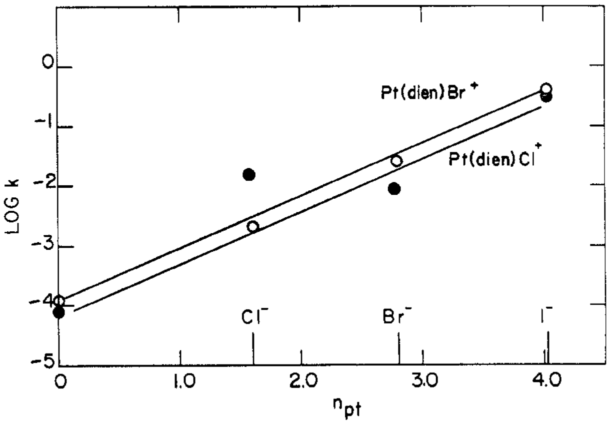

Figure 3.—The dependence of the second-order rate constant, k_Y sec^{-1} M^{-1}, upon the nucleophilic reactivity of the entering group for the halide interchange reactions of $Pt(dien)Cl^+$ (●) and $Pt(dien)Br^+$ (○) where k_Y is for 25° and is adjusted to ionic strength of zero. Points at $n_{Pt} = 0$ are k_1 sec^{-1}.

In view of the rather modest differences in extinction coefficients for the chloro and bromo complexes, $Pt(dien)X^+$, the ion-exchange and tracer technique appears to be definitely superior to spectrophotometric methods. In addition, it has the very important advantage that the concentrations of the equilibrium state can be evaluated, and an equilibrium quotient can therefore be tested over a variety of conditions. The presence of the reverse reaction does not pose the serious obstacle which is difficult to treat from spectrophotometric data. In addition, it has permitted an evaluation of the equilibrium quotient for the aquation of the complex.

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Optical and Magnetic Measurements on Single Crystals of Copper(II)-Doped Tris(phenanthroline)zinc(II) Nitrate Dihydrate

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The electron paramagnetic resonance spectrum in single crystals of copper(II)-doped tris(phenanthroline)zinc(II) nitrate dihydrate has been observed between 4 and 350°K. The results have been interpreted in terms of a Jahn–Teller effect for the copper(II) ion. At 350°K the spectrum is nearly isotropic with $g = 2.13$ and no observed hyperfine splitting. At 77°K anisotropy of the g tensor is observed with $g_{\parallel} = 2.273$, $g_{\perp} = 2.064$, $A = 160 \times 10^{-4}\ cm^{-1}$, $B < 7 \times 10^{-4}\ cm^{-1}$, $A' = 12.5 \times 10^{-4}\ cm^{-1}$, and $B' = 10.5 \times 10^{-4}\ cm^{-1}$. No significant change in the spectrum was observed at temperatures below 77°K. The optical d–d transitions and their polarization properties are reported. Two bands are observed at 7000 and 14,900 cm^{-1}. The 14,900-cm^{-1} band is split at 77°K into components at 14,700 and 15,200 cm^{-1}. The optical axes do not coincide with the principal magnetic axes.

Introduction

Electron paramagnetic resonance measurements on some tris complexes of copper(II) were reported recently[2] in which the magnetic parameters were obtained from polycrystalline samples of the copper(II) complexes in a matrix of the corresponding diamagnetic zinc(II) complex. The temperature variation of the epr spectra suggested that these complexes were ex-

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(1) (a) National Bureau of Standards; (b) University of Maryland.

(2) H. C. Allen, Jr., G. F. Kokoszka, and R. G. Inskeep, *J. Am. Chem. Soc.*, **86**, 1023 (1964).