trans-Dibromodiammineplatinum(II).   Aquation and Isotopic Exchange of Bromide Ligands with Free Bromide and with Tetrabromoplatinate(II)

BY WILLIAM H. JOLLEY, EDWARD D. SMITH, DON S. MARTIN,* JON C. CLARDY, AND JOE D. WOODS

The rate constant and equilibrium quotient for the first aquation of *trans*-Pt(NH₃)₂Br₂ have been determined by pH titration techniques. At 25° and an ionic strength of 0.05 M the equilibrium quotient was found to be $3.06 \times 10^{-5}\ M$ with $\Delta H° = 8.5$ kcal/mol. The specific aquation rate constant at 25° was $1.1 \times 10^{-3}\ \text{sec}^{-1}$. No evidence was found for a measurable second aquation reaction. The identity of the preparation was confirmed by X-ray diffraction. The isotopic exchange of bromide followed the rate law $R = [\text{Pt}(\text{NH}_3)_2\text{Br}_2](k_1 + k_{\text{Br}}[\text{Br}])$ where k_1 agreed with the measured aquation rate constant, and at 25° and $\mu = 0.05\ M$, $k_{\text{Br}} = 1.76 \times 10^{-1}\ M^{-1}\ \text{sec}^{-1}$. Upon the addition of $\text{PtBr}_4{}^{2-}$ it was shown that $\text{PtBr}_4{}^{2-}$ and $\text{Pt}(\text{NH}_3)_2\text{Br}_2$ exchanged bromide ligands without a Br^- intermediate. The rate constant for the ligand trading process at 15° was $3 \times 10^{-1}\ M^{-1}\ \text{sec}^{-1}$.

Introduction

Recent studies have indicated that the replacement of halide ligands in complexes of platinum(II) occur by several mechanisms.[1] In at least two instances the rate expressions for the bromide exchange required dimeric transition states.[2,3] The considerably different behavior observed between $\text{PtBr}_4{}^{2-}$ and Pt(dien)-Br⁺ was possibly attributable to the cis bromides in $\text{PtBr}_4{}^{2-}$. The present work was undertaken to examine another bromide system in which there were no cis bromides. The possible mutual influence of Pt-Br₄²⁻ upon the bromide exchange was also investigated.

A characterization of the isotopic exchange requires a correlation with the kinetics of the reversible aquation of the bromide ligands, and an investigation of this process was included. When these studies indicated that a measurable replacement of only one bromide ligand per platinum occurred, an X-ray diffraction crystal structure determination was performed to confirm the identity of the complex.

Experimental Section

Preparation and Characterization of *trans*-Pt(NH₃)₂Br₂.—The stable salt, K₂PtBr₆, which had previously been purified from iridium impurity,[4] was reduced to Pt(II) by heating with an equimolar amount of potassium oxalate in solution. A small amount of unreacted salt was filtered off the cold solution. The $\text{PtBr}_4{}^{2-}$ in the solution was converted to the colorless tetraammineplatinum(II) complex by a slight excess of concentrated ammonia solution. Small amounts of concentrated HBr were added slowly with stirring and warming. After about 10 min the solution became pale yellow and the *trans*-Pt(NH₃)₂Br₂ was deposited as a fine pale yellow powder. The powder was filtered from the solution repeatedly since prolonged contact with the solution produced some tribromoammineplatinate(II) ion. After these successive amounts were collected they were washed thoroughly with warm water. Because of its extreme insolubility and its precipitation from a homogeneous medium, additional purification was not necessary. Recrystallization from *N,N*-dimethylformamide, in which it is readily soluble, did not alter its absorption spectrum.

Because of the unexpected behavior that only one hydrolysis step could be detected for the preparation, special attention was given to its analyses. *Anal.* Calcd for *trans*-Pt(NH₃)₂Br₂: C, 0.00; N, 7.20; H, 1.56. Found: C, 0.01; N, 7.14; H, 1.75. Residue from thermogravimetric analysis: platinum, calcd 50.1,
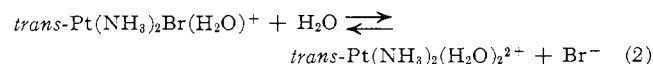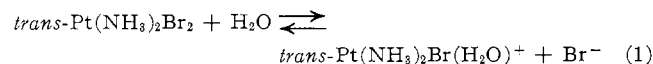
found 50.2; Br⁻ (gravimetric as AgBr), calcd 41.1, found 40.1. (This low value was likely due to loss of AgBr precipitate.)

Finally, a full crystal structure analysis by X-ray diffraction was performed. From rotation and Weissenberg photographs the crystal was determined to be monoclinic and belong to space group $P2_1/c$. From a density of *ca.* 3.6 g cm⁻³, inferred from the floatation method with a concentrated aqueous solution of zinc iodide, two molecules per unit cell were required. Accurate X-ray diffraction data for approximately 2000 reflections were collected by a diffractometer. The unit cell dimensions were $a = 5.711$ (3) Å, b (unique axis) $= 6.318$ (3) Å, $c = 8.277$ (3) Å, $\beta = 95.5$ (5)°. The structure was found to be very similar to that reported by Milburn and Truter[5] for *trans*-Pt(NH₃)₂Cl₂; and, consequently, it was refined without absorption correction only to a present value of 13% for R. The position of the molecule at a center of symmetry confirmed the planarity and a trans isomer. With a platinum atom at the origin the parameters for the atomic locations, x/a, y/b, z/c, of N are 0.2034 (3), −0.1694 (3), and 0.1782 (3) and of Br are 0.2814 (3), 0.2928 (3), and 0.0256 (3). The Pt–Br and Pt–N bond distances are 2.45 (1) and 2.08 (1) Å, respectively, and bond angles are 89.5 (5) and 90.5 (5)°.

An absorption spectrum for a solution of the preparation is shown in Figure 1. The spectrum was obtained with KBr added to suppress aquation; the reference cell contained an equal concentration of KBr. The accuracy in the molar absorptivity was limited by the very low solubility of the compound and by absorption at the lower wavelengths by bromide ion. Two peaks were at 30,200 cm⁻¹ (330 nm) and 35,000 cm⁻¹ (286 nm). The peak at higher energy was displaced somewhat to longer wavelengths from the two reported at 335 and 276 nm by Babaeva and Lapir[6] in 1949. Although the molar absorptivity of the peak at 330 nm agreed satisfactorily with their long-wavelength peak, their spectrum indicated a significantly higher absorption at shorter wavelengths. They commented that a few drops of HBr were added to stabilize the solution and it seems likely that their higher absorption was due to Br⁻ which was not balanced in a reference cell.

Other materials were of analytical reagent grade. Demineralized water which had been distilled from alkaline permanganate was used throughout.

Procedures. A. Aquation Rate and Equilibrium Quotient.—The *trans*-Pt(NH₃)₂Br₂ was expected to undergo replacement of Br⁻ ligands by H₂O according to the reactions

$$\textit{trans-}\text{Pt}(\text{NH}_3)_2\text{Br}_2 + \text{H}_2\text{O} \rightleftharpoons$$
$$\textit{trans-}\text{Pt}(\text{NH}_3)_2\text{Br}(\text{H}_2\text{O})^+ + \text{Br}^- \quad (1)$$

$$\textit{trans-}\text{Pt}(\text{NH}_3)_2\text{Br}(\text{H}_2\text{O})^+ + \text{H}_2\text{O} \rightleftharpoons$$
$$\textit{trans-}\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2{}^{2+} + \text{Br}^- \quad (2)$$

It is generally possible to titrate one acidic proton for an H₂O ligand on a platinum(II) complex. For such titrations, a Radiometer Automatic Titrator, Model ABU1c-TTA3-SBR2C, was em-

(1) D. S. Martin, Jr., *Inorg. Chim. Acta Rev.*, **1**, 87 (1967).

(2) J. E. Teggins, D. R. Gano, M. A. Tucker, and D. S. Martin, *Inorg. Chem.*, **6**, 69 (1967).

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

(4) L. S. Jowanovitz, F. B. McNatt, R. E. McCarley, and D. S. Martin, Jr., *Anal. Chem.*, **32**, 1270 (1960).

(5) G. H. W. Milburn and M. R. Truter, *J. Chem. Soc. A*, 1609 (1966).

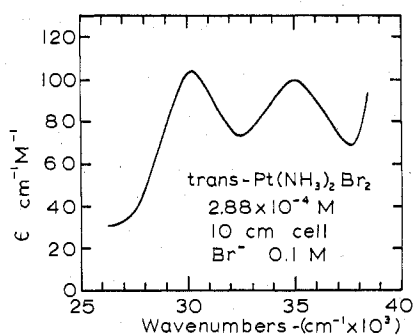(6) A. V. Babaeva and E. S. Lapir, *Dokl. Akad. Nauk SSSR*, **64**, 679 (1949).

Figure 1.—Absorption spectrum for an aqueous solution of *trans*-Pt(NH₃)₂Br₂.

ployed. To evaluate equilibrium quotients, direct titrations of equilibrium solutions by sodium hydroxide were performed. Standard aqueous solutions of the complex in the range of 0.05–0.30 mM were prepared by direct weighing. Dissolution required 15–24 hr of constant stirring. The ionic strength of each solution was adjusted to 0.05 M by the addition of NaNO₃. Solutions were equilibrated in a thermostated bath with control to ±0.05°. Aliquots were rapidly withdrawn from the equilibrated solution by pipet and titrated in a thermostated glass vessel with a glass indicator electrode. The titrations required less than 60 sec, so no substantial aquation of the complex occurred during the course of the titration.

Considerable difficulty was experienced in the titrations because of the very low concentrations of solutions which were required. The low solubility of the complex (approximately 0.01 g/100 ml at 25°) necessitated the use of a low alkali concentration of approximately 0.01 M which in turn was standardized with a 10⁻⁴ M standard potassium hydrogen phthalate solution. In a titration, to determine the true value of the titer, allowance had to be made for the amount of NaOH solution to raise the pH of the solution to the equivalence point. This was accomplished by titrating "blank" solutions of 0.05 M NaNO₃ to pH 7.1 and 7.7 corresponding to the equivalence points of phthalate and complex titrations. By subtracting the blanks from the total titer,

TABLE I
DETERMINATION OF THE AQUATION EQUILIBRIUM QUOTIENT FROM TITRATION OF EQUILIBRIUM SOLUTIONS (IONIC STRENGTH 0.05 M; $\Delta H°$ = 8.5 ± 0.5 KCAL/MOL)

Total complex [Pt], mM	Titer [*trans*-[Pt(NH₃)₂Br(H₂O)]⁺], mM	Equilibrium quotient K_1, mM
	15°	
0.0531	0.0236 ± 0.0013	0.0188
0.0986	0.0344 ± 0.0013	0.0184
0.1517	0.0436 ± 0.0013	0.0176
0.1972	0.0503 ± 0.0013	0.0188
		Av 0.0178 ± 0.0003
	25°	
0.0502	0.0270 ± 0.0023	0.0315
0.0984	0.0458 ± 0.0023	0.0399
0.1355	0.0522 ± 0.0023	0.0327
0.2018	0.0673 ± 0.0023	0.0337
0.2195	0.0655 ± 0.0023	0.0279
0.2994	0.0795 ± 0.0023	0.0287
0.2995ᵃ	0.0510 ± 0.0023	0.0264
0.3054	0.0783 ± 0.0023	0.0270
0.3987	0.0963 ± 0.0023	0.0307
		Av 0.0306 ± 0.0009
	35°	
0.0984	0.0507 ± 0.0018	0.0538
0.1355	0.0647 ± 0.0018	0.0591
0.2018	0.0755 ± 0.0018	0.0451
0.2195	0.0799 ± 0.0018	0.0457
0.2994	0.0945 ± 0.0018	0.0436
0.3054	0.0957 ± 0.0018	0.0437
		Av 0.0455 ± 0.0022

ᵃ 77.5 mM Br⁻ added.

the true titer for the species being titrated could be obtained. The results of these titrations are included in Table I. Generally each titer was the average of 5–8 experiments. The indicated uncertainties in the titer included the contributions from the blanks and the standardizations as well.

Rates of aquation were determined by means of pH-stat procedures. Sodium hydroxide solution was automatically added to an aliquot of a complex solution to maintain it at a somewhat higher pH than the equivalence point. The pH was maintained at 8.5 for the majority of these experiments but in several a value of 9.5 was used to detect a possibly weaker acid component. In such an experiment there was typically a rapid addition of alkali, which amounted to 20–25% of that eventually required and which served to raise the pH of the solution to the operating value and to neutralize the acid of any aquo ligands which were present at the start of the experiment. Generally, such aquation was suppressed by the addition of bromide ion. All titrations were performed with 15- or 20-ml samples and the maximum alkali solution added was 0.25 ml. Hence the volume of the solution did not change significantly throughout an experiment. The titration vessel was covered with black opaque tape to exclude light. After the initial addition of base, the rate of addition, which was required to neutralize the aquo species as it formed, corresponded to the rate of aquation.

B. Exchange Studies.—The radioactive nuclide ⁸²Br, utilized for the isotopic exchange studies, was prepared and counted by the procedures described previously.[3]

For the system *trans*-Pt(NH₃)₂Br₂–Br⁻ an anion-exchange column seemed a likely choice for the separation of *trans*-Pt-(NH₃)₂Br₂ and Br⁻ which is required for an exchange experiment. Grinberg and Shagisultanova in a brief study[7] commented on the difficulty of this separation which we have confirmed. In principle, bromide should be retained by an ion exchanger whereas the neutral complex as well as the cation, Pt(NH₃)₂Br(H₂O)⁺, should be quickly eluted. The method was used successfully for the *cis*- and *trans*-Pt(NH₃)₂Cl₂ systems.[8] However, with the bromide systems there is a very high retention of the platinum complex. Very careful control of conditions are required to gain sufficient retention of bromide and still attain sufficient and reproducible elution of the complex. Conditions are especially critical since half-times in some instances were only a few minutes. To initiate an exchange experiment between *trans*-Pt(NH₃)₂Br₂ and Br⁻, a small amount of the tracer solution, 10–50 µl, was added to 30 ml of the reaction solution in a flask with an opaque wrapping. At intervals, 2.00-ml samples were rapidly withdrawn from the flask and quickly run through separate anion-exchange columns. The columns were 1.5 cm in diameter and 15 cm long, packed to a 6.5 cm depth with Rohm and Haas IRA 400 anion-exchange resin in the nitrate form. This resin was replaced after each use. The complex was therefore separated rapidly from the bulk of the bromide ion. The column was then washed immediately with 200 ml of water to elute the uncharged species and any cationic aquo species. Tests indicated that the order of 0.1% of the Br⁻ was eluted. For each exchange experiment, at least three samples were collected at sufficiently long times that isotopic equilibrium had been established. In addition, samples of the reaction solution were withdrawn for counting without the ion-exchange column separation in order to determine the total ⁸²Br activity. To each of the eluted solutions were added approximately 0.25 g of KBr and 0.25 g of KOH. The KOH was added to prevent loss from volatility of HBr since the samples were reduced in volume to 10–15 ml by boiling. The samples were added to plastic counting vials and diluted to a 25 ml volume for reproducible counting geometry.

The fraction of exchange, F_i, for the sample collected at time t_i, was calculated for each sample from the equation

$$F_i = C_i/C_\infty \qquad (3)$$

where C_i and C_∞ are the counting rates at t_i and the infinity time, respectively. The plot of log $(1 - F)$ *vs.* time for a typical exchange is shown in Figure 2. The fraction recovery of complexed bromide was determined from the infinity counting rates, the counting rate of an unseparated sample, and the concentration of complex and bromide. Although this was somewhat variable

(7) A. A. Grinberg and G. A. Shagisultanova, *Radiokhimiya*, **2**, 592 (1960).
(8) (a) J. W. Reishus and D. S. Martin, Jr., *J. Amer. Chem. Soc.*, **83**, 2457 (1961); (b) D. S. Martin, Jr., and R. J. Adams, "Advances in Chemistry," S. Kirshner, Ed., Macmillan, New York, N. Y., 1961, p 579.
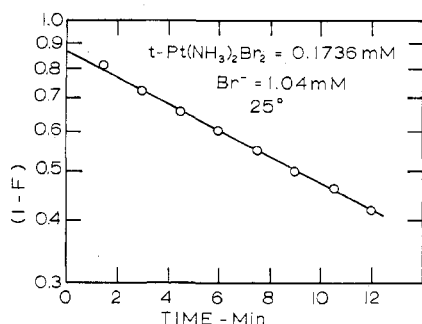
Figure 2.—Semilogarithmic plot of $(1 - F)$ vs. time for a representative exchange experiment.

between experiments, a group of columns packed together with one batch of resin usually performed consistently as indicated by grouping of points around the line in Figure 2. The intercept of the curve is presumed to represent the leakage of bromide through the column which again was fairly reproducible. Although the separation procedure was not perfect in that some bromide penetrated the columns and some of the complex was retained, it provided a satisfactory control of these factors so that significant results were obtained.

The influence of the presence of $PtBr_4^{2-}$ upon the rate at which ^{82}Br entered the *trans*-$Pt(NH_3)_2Br_2$ was studied. There were two series of experiments. For the first series both Br^- and $PtBr_4^{2-}$ were tagged initially with identical specific activities. The exchange solutions were prepared in two portions. The first portion contained the *trans*-$Pt(NH_3)_2Br_2$, KBr, Rb_2PtBr_4, and $NaNO_3$ which was allowed to equilibrate in the dark. The second portion contained the same concentrations of KBr, Rb_2PtBr_4, and $NaNO_3$ and the tagged $^{82}Br^-$. The second portion was allowed to attain isotopic equilibrium before it was added to the first portion to initiate the exchange reaction with *trans*-$Pt(NH_3)_2Br_2$. Samples were withdrawn, and following ion exchange separation the value of F_i was determined for the *trans*-$Pt(NH_3)_2Br_2$ fraction as described above. In this type of experiment active bromide could come from either free Br^- or $PtBr_4^{2-}$.

In a second series of experiments a solution of *trans*-$Pt(NH_3)_2Br_2$, KBr, Rb_2PtBr_4, and $NaNO_3$ in a flask was permitted to attain aquation equilibrium in the dark. To this flask was added the $^{82}Br^-$ tracer to initiate the exchange. Aliquots for separation and analysis were withdrawn as before. For the infinite-time samples a period of at least 24 hr was required for the $PtBr_4^{2-}$ to attain isotopic equilibrium. The rate of exchange between *trans*-$Pt(NH_3)_2Br_2$ and Br^- was inferred from the slope, (dC_i/dt), at zero time when active ^{82}Br could only enter from the Br^- ion and not from the $PtBr_4^{2-}$.

For the evaluation of the rate of introduction of tagged bromide into $PtBr_4^{2-}$, the $PtBr_4^{2-}$ was precipitated by the tetraphenylarsonium cation following the procedure of Teggins, *et al.*[2] The specific activities of the precipitates were determined by weighing the deposit on a tared filter paper and then counting the ^{82}Br with the scintillation spectrometer.

Although exchange in the *trans*-$Pt(NH_3)_2Br_2$ system was measured at 15° and 25° the rates were so high that the influence of $PtBr_4^{2-}$ upon the exchange could not be studied above 15°. At lower temperatures the solubility of the *trans*-$Pt(NH_3)_2Br_2$ was too low for satisfactory results.

Results and Discussion

Aquation Reaction of the *trans*-$Pt(NH_3)_2Br_2$.—The titration data of the equilibrium solutions in Table I were collected with the expectation that the equilibrium quotients K_1 and K_2 for the reactions in eq 1 and 2 could be evaluated. If one proton from each aquo ligand is titrated the total titer for an equilibrated solution is related to the equilibrium quotients, K_1 and K_2, by the expression[9]

$$K_1(b + T)(a - T) + K_1K_2(2a - T) =$$
$$T(b + T)^2 \quad (4)$$

(9) C. I. Sanders and D. S. Martin, Jr., *J. Amer Chem. Soc.*, **83**, 807 (1961).

where a = the total concentration of platinum in the three complexes, and b = the concentration of added bromide.

Equation 4 is a cubic equation in T, and the variable parameters K_1 and K_2 were found from an iterative weighted least-squares procedure. It was found however that no statistically significant better fit to the data was obtained with the two constants than when only a single constant K_1 was used with K_2 set equal to zero. The data therefore implied that the second aquation, reaction 2, occurred to an undetectable extent or that it was so slow that the equilibration time of several days was too small for an appreciable reaction to have occurred.

The pH-Stat experiment provided further evidence that only reaction 1 was effectively involved. The alkali consumed when the curve had approached an asymptotic limit corresponded within the experimental error to 1 equiv/platinum. The experiments were extended for 15 hr. Most were at a pH of 8.5, although a few were at 9.5, well above the titration end point of 7.7. Therefore, the quotient, K_2, was placed equal to zero in eq 4, which was then utilized for the computation in K_1 from the measured titers. Results are in Table I where the weighted average values of K_1 at each temperature and the indicated $\Delta H°$ are included. The individual values of K_1 were weighted with the factor $(K_1/\sigma_{K_1})^2$ where the σ_{K_1} was propagated from the individual values of the indicated standard deviations in T, the titer.

The aquation rates for *trans*-$Pt(NH_3)_2Br_2$ were obtained from the pH-Stat experiments in which the base, consumed in neutralizing the acidic protons of the aquo ligands as they formed, was recorded as a function of time. Guggenheim plots[10] over several half-periods were prepared. The indicated rate constants, are included in Table II. The kinetic parameters $\Delta H^{\ddagger}$ of

TABLE II

RATE CONSTANTS FOR THE AQUATION AND ISOTOPIC
EXCHANGE REACTIONS OF *trans*-$Pt(NH_3)_2Br_2$

Temp, °C	$10^5 k_1$,[a] sec^{-1}	k_{-1},[b] M^{-1} sec^{-1}	$10^2 k_{Br}$, M^{-1} sec^{-1}	k_{ac}, M^{-1} sec^{-1}
15	0.35 ± 0.02 (0.49 ± 0.08)	20 ± 2	9.0 ± 0.7	0.32
25	1.07 ± 0.08 (1.40 ± 0.20)	35 ± 3	17.6 ± 2.5	
35	2.88 ± 0.05	62 ± 1		
$\Delta H^{\ddagger}$, kcal/mol	18.0 ± 0.5	9.5 ± 0.9	10.9	
$\Delta S^{\ddagger}$, cal/deg mol	-12 ± 2	-20 ± 2	-25.3	

[a] Values in parentheses are from exchange experiments. Values without parentheses are from pH-Stat experiments. [b] From the values of k_1 and the equilibrium quotients, K_1.

18.0 kcal/mol and $\Delta S^{\ddagger}$ of -12 cal/deg mol are similar to those of substitution of a number of platinum(II) complexes.[11]

Exchange between *trans*-$Pt(NH_3)_2Br_2$ and Br^-.—The collection of data for exchange experiments at 15 and 25° is presented in Table III. From the aquation equilibrium quotients it can be calculated that the *trans*-$Pt(NH_3)_2Br(H_2O)^+$ species constitute only 3% of the total complex concentration at the lowest bromide concentration, 1.0 mM. Under these conditions

(10) A. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

(11) U. Belluco, R. Ettore, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

TABLE III

ISOTOPIC EXCHANGE OF ^{82}Br BETWEEN
trans-Pt(NH$_3$)$_2$Br$_2$ AND Br$^-$

[*trans*-Pt(NH$_3$)$_2$Br$_2$], M	[Br$^-$], mM	10^7R, M sec^{-1}
	15°	
0.443	1.04	0.304
0.443	1.04	0.305
0.457	1.04	0.404
0.887	1.04	0.527
1.329	1.04	0.646
1.330	1.04	0.662
1.331	1.04	0.825
1.336	1.04	0.671
1.772	1.04	0.898
1.772	1.04	0.980
1.390	6.02	1.52
1.854	6.07	1.68
1.350	11.05	1.93
1.857	16.07	3.55
1.351	16.12	2.72
1.610	21.03	4.16
1.859	21.05	4.44
1.610	26.04	4.65
1.859	26.04	4.81
	25°	
0.196	1.04	0.404
0.211	1.04	0.365
0.502	1.04	0.825
0.587	1.04	1.12
0.657	1.04	0.815
0.876	1.04	1.19
1.159	1.04	1.53
1.314	1.04	1.89
1.367	1.04	1.73
1.367	1.04	1.81
1.367	1.04	1.82
1.453	1.04	1.90
1.736	1.04	2.60
1.753	1.04	2.45
1.939	1.04	2.82
1.972	1.04	2.40
1.973	1.04	2.44
2.083	1.04	2.55
2.094	1.04	3.11
1.793	6.03	4.25
1.407	10.02	4.59
1.348	11.02	4.47
1.350	16.03	5.68
1.250	16.1	6.13
1.350	21.03	6.69
1.407	25.10	7.14
1.350	26.04	8.34

the rate of exchange can be inferred by the application of the McKay equation.[12]

$$R_{ex}t_i(2a + b)/2ab = \ln (u_\infty - u_i)/u_\infty \quad (5)$$

where u_i, u_∞ are the concentrations of the tracer isotope in *trans*-Pt(NH$_3$)$_2$Br$_2$ at time t_i and infinite time, respectively (counts min^{-1} ml^{-1}), R_{ex} is the exchange rate (M sec^{-1}), a is the concentration of Pt(NH$_3$)$_2$Br$_2$ (M) and b is the concentration of Br$^-$ (M).

In an exchange experiment the counting rate C_i, from an aliquot collected at t_i, is

$$C_i = V[(I - u_i) f_b + u_i f_a] \quad (6)$$

where V is the volume of the aliquot (ml), I is the concentration of total radioactivity (counts min^{-1} ml^{-1}), and f_b, f_a are the fractions of bromide ion and *trans*-Pt-(NH$_3$)$_2$Br$_2$, respectively, which are collected from the
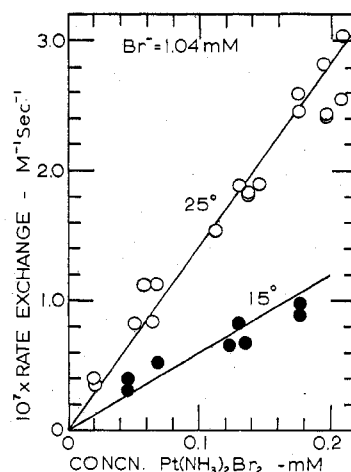
(12) H. McKay, *Nature (London)*, **142**, 997 (1938).

Figure 3.—Rate of exchange of ^{82}Br between *trans*-Pt(NH$_3$)$_2$Br$_2$ and Br$^-$ *vs.* the concentration of *trans*-Pt(NH$_3$)$_2$Br$_2$. Ionic strength = 0.050 M.

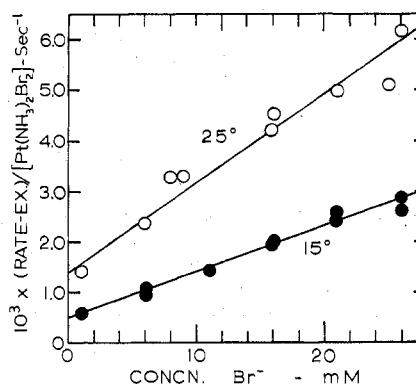Figure 4.—Bromide dependence for the exchange rate between Br$^-$ and *trans*-Pt(NH$_3$)$_2$Br$_2$.

ion-exchange column for the counting sample. From this equation it follows that

$$\ln (1 - u_i/u_\infty) = \ln (1 - C_i/C_\infty) +$$
$$\ln [1 + If_b/(f_a - f_b)u_\infty] \quad (7)$$

Since the last term is a constant, the rate of exchange is given by the equation

$$R_{ex} = \frac{2ab}{(2a + b)} \frac{d}{dt} \ln (1 - C/C_\infty) \quad (8)$$

The rates given in Table III were obtained from the least-squares slopes of the plots of $\ln (1 - C/C_\infty)$.

The plot of the exchange rate *vs.* [*trans*-Pt(NH$_3$)$_2$-Br$_2$] for [Br$^-$] of 1.04 mM is given in Figure 3. At this lowest bromide concentration the greatest contribution of a term, second order in complex, can be expected.[3] The good linear plots indicate that in this system, unlike that for PtBr$_4^{2-}$, there is no contribution from a mechanism which requires a dimeric transition state.

The plots of $R_{ex}/$[*trans*-Pt(NH$_3$)$_2$Br$_2$] *vs.* [Br$^-$] are shown in Figure 4. The data are consistent with the rate law which has been found for many ligand substitution reactions of platinum(II)

$$R_{ex} = [trans\text{-Pt(NH}_3)_2\text{Br}_2](k_1 + k_2[\text{Br}^-]) \quad (9)$$

The rate constants from a least-squares treatment of the plots in Figure 4 are included in Table II. Gen-

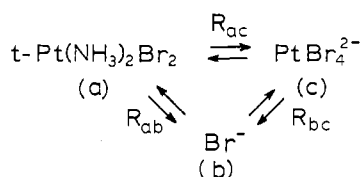$$t\text{-}Pt(NH_3)_2Br_2 \underset{\phantom{R_{ac}}}{\overset{R_{ac}}{\rightleftarrows}} PtBr_4^{2-}$$

Figure 5.—Scheme for exchange in the three-component system.

erally, the first-order rate constant, k_1, is considered to describe the solvation of the complex followed by a replacement of the solvent by the entering ligand. The agreement between the values of k_1 inferred from the exchange and from the pH-Stat determination is sufficiently good in view of the experimental uncertainty to confirm this mechanism. The comparison of the chloride and bromide system is, of course, of interest. The aquation equilibrium quotient, K_1, at 25° for *trans*-Pt(NH_3)_2Br_2 is only one-tenth the value for *trans*-Pt(NH_3)Cl_2 reported by Adams and Martin[8b] although a part of the difference can be attributed to the lower ionic strength of the present work. The $\Delta H°$ is 3.0 kcal/mol higher for the bromide system. The aquation rate constant, k_1, for *trans*-Pt(NH_3)_2Br_2 should be relatively insensitive to ionic strength and is a factor of 10 higher for the bromide system than for the chloride. The difference in the activation enthalpy in the two systems was not more than 1.0 kcal and probably the two $\Delta H^{\ddagger}$ can be considered equal within the experimental uncertainty. The results are not in agreement with those of Makashev, *et al.*,[13] who reported a k_1 at 25° of 1.4×10^{-5} sec^{-1} from combined conductivity–pH measurements of a 2.3×10^{-5} M solution. Their numerical data were not reported. From the plot of conductivity presented for 25° it can be seen that their first conductivity measurement was recorded 40 min after the start of the reaction and that the change in conductance recorded was not large in comparison to the uncertainty in their equilibrium measurements. Modest increases in the aquation rates at 25° of the bromide ligand over those for chloride have been noted for the other platinum(II) complexes, PtX_4^{2-} and Pt(dien)X$^+$, where dien is diethylenetriamine.[3,4,14]

The direct nucleophilic attack of bromide, as indicated by k_2, is faster by a factor of 200 than the corresponding chloride reaction. The activation enthalpy, $\Delta H^{\ddagger}$ for bromide is only 10.9 kcal/mol in contrast to 20 kcal for chloride.

Isotopic Exchange in the System Br$^-$–*trans*-Pt(NH_3)_2Br_2–PtBr_4^{2-}.—In this three-component system there may be an isotopic exchange process between each pair of components as indicated in Figure 5. However, there is a possibility that each of these indicated rates may be influenced, *i.e.*, catalyzed, by the presence of the component not involved in the indicated process. Thus, Teggins and Martin concluded that PtBr_4^{2-} and Pt(dien)Br$^+$ each catalyzed the exchange of the other complex with Br$^-$.[4] If both Br$^-$ and PtBr_4^{2-} are initially tagged with ^{82}Br and if, in addition, the concentration of each is considerably greater than that of *trans*-Pt(NH_3)_2Br_2, then an extension of eq 8 provides the following expression which applies for the amount of activity in *trans*-Pt(NH_3)_2Br_2.

(13) Yu. A. Makashev, F. Ya. Kul'ba, R. A. Zlotnikova, and A. A. Korableva, *Zh. Neorg. Khim.*, **15**, 3294 (1970).

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$$\ln (1 - C_t/C) = (R_{ab} + R_{ac})t_i/2a \quad (10)$$

The results of a series of exchange experiments at 15° are given in Table IV. The sum of rates, $(R_{ab} + R_{ac})$,

TABLE IV
ISOTOPIC EXCHANGE REACTIONS FOR
Pt(NH_3)_2Br_2 WITH Br$^-$ AND PtBr_4^{2-} TAGGED INITIALLY[a]

[PtBr_4^{2-}], mM	$\tau_{1/2}$, min	$10^7(R_{ao} + R_{ab})$, M sec^{-1}	$10^7(R_{ao} + R_{ab} - R_{ab}°)$, M sec^{-1}
0	13.8 ± 0.8	2.5 ± 0.1	
1.0	11.1 ± 0.5	3.1 ± 0.1	0.6 ± 0.2
2.0	10.4 ± 0.5	3.3 ± 0.2	0.8 ± 0.3
3.0	9.0 ± 0.6	3.8 ± 0.3	1.3 ± 0.3
4.0	8.2 ± 0.4	4.2 ± 0.2	1.7 ± 0.3
5.0	7.1 ± 0.5	4.9 ± 0.3	2.4 ± 0.3

[a] Ionic strength = 0.05 M, 15°, [*trans*-Pt(NH_3)_2Br_2] = 0.15 mM, [Br$^-$] = 12.5 mM.

was calculated from the half-time of the reaction. It can be seen from the data in the table that the rate of introduction of active bromide into the Pt(NH_3)_2Br_2 is nearly doubled by the addition of 5 mM PtBr_4^{2-} which is tagged.

For the situation in which the PtBr_4^{2-} was not tagged initially, the rate R_{ab} can be inferred from the initial slope of the plot of C_i vs. time. It should be noted that the ratio C_i/C_∞ cannot be considered as a "fraction of exchange" in such a three component system. If, for example, $R_{ab} > R_{bc}$, C_i/C_∞ will rise rapidly to a value greater than one and will approach one from the positive side as the PtBr_4^{2-} approaches isotopic equilibrium. However, in determining the exchange rate, R_{ab}, consideration must be given to the efficiencies for the ion-exchange separation. The rate, R_{ab} is given by the expression
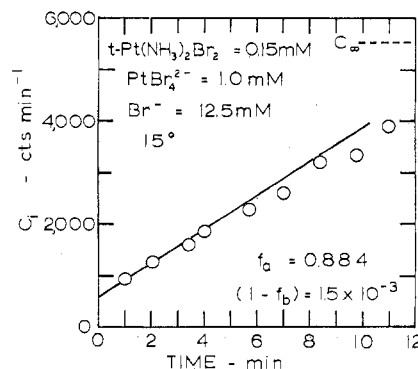
$$R_{ab} = (b/I)(du/dt)_{t=0} \quad (11)$$

From eq 6 it appears that

$$(du/dt)_0 = [(1/V(f_a - f_b)](dC_i/dt)_0 \approx (1/Vf_a)(dC_i/dt)_0 \quad (12)$$

Therefore the rates were calculated from the initial slopes of plots of (dC_i/dt) by the expression

$$R_{ab} = (b/IVf_a)(dC_i/dt)_0 \quad (13)$$

Results of such an experiment are shown in Figure 6, and the collection of results for 15° are included in Table V. It can be seen from these data that the exchange rate, R_{ab}, is not substantially changed by the

Figure 6.—Introduction of ^{82}Br tracer into *trans*-Pt(NH_3)_2Br_2 from Br$^-$ in the presence of untagged PtBr_4^{2-}.

TABLE V

ISOTOPIC EXCHANGE OF BROMIDE BETWEEN
trans-Pt(NH₃)₂Br₂ AND Br⁻ IN THE PRESENCE OF UNTAGGED
PtBr₄²⁻ ᵃ

[PtBr₄²⁻] added, mM	% elution of complex	$10^7 R_{ab}$, M sec⁻¹	[PtBr₄²⁻] added, mM	% elution of complex	$10^7 R_{ab}$, M sec⁻¹
0.5	70	2.6	2.0	86	3.6
1.0	89	3.0	2.0	78	2.3
1.0	84	2.7	2.5	84	3.7
1.0	85	2.4	3.0	65	1.9
1.0	89	2.1	3.0	86	3.6
1.5	80	2.5	3.0	85	2.7
2.0	65	2.8	4.0	86	3.0
2.0	78	2.4	5.0	79	3.3
					Av 2.7 ± 0.6

ᵃ Ionic strength 0.05 mM, [*trans*-Pt(NH₃)₂Br₂] = 0.15 mM, [Br⁻] = 12.5 mM, at 15°.

additions of PtBr₄²⁻. Therefore, since the sum of rates $R_{ab} + R_{ac}$ had approximately doubled by the addition of 5 mM PtBr₄²⁻, it must be concluded that the two complexes *trans*-Pt(NH₃)₂Br₂ and PtBr₄²⁻ are exchanging or "trading" ligands directly. The system is therefore different from the Pt(dien)Br⁺–PtBr₄²⁻ where it was concluded[3] that the exchange of each complex with bromide was catalyzed without substantial ligand trading. The ligand trading rate is seen from the data in Table V to be proportional to the concentration of PtBr₄²⁻. Presumably, it is also proportional to the concentration of *trans*-Pt(NH₃)₂Br₂ and the rate constant at 15° for the trading, k_{ac}, is about 0.32 M^{-1} sec⁻¹. At this temperature the second-order rate constant is at least 7 times higher than the rate constant for ligand exchange catalysis found for the Pt(dien)-Br⁺–PtBr₄²⁻ systems.

Upon the completion of these results it was apparent that the trading of ligands between *trans*-Pt(NH₃)₂Br₂ and PtBr₄²⁻ would substantially influence the rate at which PtBr₄²⁻ approached isotopic equilibrium. The *trans*-Pt(NH₃)₂Br₂, which is present in so much smaller amounts than PtBr₄²⁻, approaches isotopic equilibrium with Br⁻ with a half-life which is an order of magnitude smaller than that for PtBr₄²⁻. Therefore the plot of log $(1 - F_i)$ for PtBr₄²⁻ was a linear function of time, from which the half-life could be determined. The rate of exchange, which will be $(R_{bc} + R_{ac})$ was calculated from the expression

$$(R_{bc} + R_{ac}) = \frac{(\ln 2)4c(b + 2a)}{\tau_{1/2}(b + 2a + 4c)} \qquad (14)$$

This equation neglects the extent of aquation for the two complexes. Since the separation method precipitates PtBr₄²⁻ and PtBr₃(H₂O)⁻ together, the bromides in these two species comprise one fraction. From the aquation equilibrium constant for PtBr₄²⁻, only 3% of the bromide ligands in this fraction are replaced by H₂O and eq 14 is satisfactory to describe the exchange rate for the PtBr₄²⁻–PtBr₃(H₂O)⁻ fraction.

The results of these experiments for the exchange between PtBr₄²⁻ and Br⁻ are in Table VI. Values of $R_{bc}°$, obtained in the absence of *trans*-Pt(NH₃)₂Br₂, could not be compared directly with those of Teggins, *et al.*, because of the lower ionic strength. However, the present results were consistent with their ionic strength trends and indicate that aquation of the bromide ligands served as the principal mechanism for the

TABLE VI

ISOTOPIC EXCHANGE BETWEEN PtBr₄²⁻ AND Br⁻ IN THE
PRESENCE *trans*-Pt(NH₃)₂Br₂ᵃ

[PtBr₄²⁻], mM	Half-life[b] $\tau_{1/2}°$, min	$\tau_{1/2}$, min	Rate exchange[c] $10 R_{ex}°$, M sec⁻¹	$10 R_{ex}$, M sec⁻¹	$10^7 R_{ac}$ calcd,[d] M sec⁻¹
1.0	620	370	0.5	0.9	0.5
3.0	250	190	2.8	3.8	1.4
4.0	240	165	3.4	5.0	1.9
5.0	190	130	4.7	7.0	2.4

ᵃ Ionic strength 0.05 M and [Br⁻] = 12.5 mM at 15°. ᵇ $\tau_{1/2}°$ for no *trans*-Pt(NH₃)₂Br₂, $\tau_{1/2}$ for 0.15 M *trans*-Pt(NH₃)₂Br₂. ᶜ $R_{ex}°$ for no *trans*-Pt(NH₃)₂Br₂, R_{ex} for 0.15 M *trans*-Pt(NH₃)₂Br₂. ᵈ $k_{ac} = 0.32$ sec⁻¹ M^{-1}.
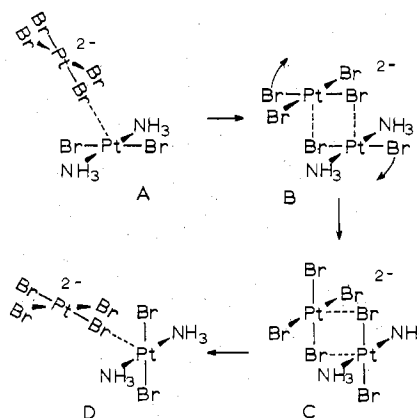

Figure 7.—Possible mechanism for the trading of bromide ligands between *trans*-Pt(NH₃)₂Br₂ and PtBr₄²⁻.

exchange at 15° and an ionic strength of 0.05 M. The presence of *trans*-Pt(NH₃)₂Br₂ reduced the half-time of the exchange significantly, and the difference in the exchange rate, $R_{ex} - R_{ex}°$, agreed satisfactorily with the calculated value of R_{ac}.

A possible mechanism for the trading of bromide ligands between the two complexes is shown in Figure 7. The first step is an attack by the bromide ligands of one complex along the axial position of the other complex to form a weak bridging bond shown in A. Rotation of the complexes will permit the formation of the two weak unsymmetric bridges as in B. The transition state is reached with symmetric bridge bonds when the two bromides trans to the bridge move according to the arrows. In such a transition state each platinum has approximately the trigonal-bipyramidal coordination which is considered typical for ligand substitution of platinum(II) complexes. It is noted that for a (dien) complex the entire chelating molecule would have to swing and such a motion, which the solvent molecules resist, must require much higher activation enthalpy.

The behavior of the *trans*-Pt(NH₃)₂Br₂ generally fits well into the pattern of behavior which is developing for the ligand substitution reactions for platinum(II) complexes. First of all, the bromide and chloride are not very different as leaving groups as evidenced by differences of not more than a factor of 10 in the aquation rates of *trans*-Pt(NH₃)₂Br₂ and *trans*-Pt(NH₃)₂Cl₂. The much greater nucleophilicity of the bromide, however, is evidenced in the higher second-order direct-substitution rate. In addition, although no anomalous behavior was evident in simple exchange behavior, the trading of ligands between *trans*-Pt(NH₃)₂Br₂ and PtBr₄²⁻ is now the fourth system to be found in which there are pairs of complexes involved in the exchange

processes for ligands.[1] Such processes appear to be quite common in bromide systems and may reflect the greater stability of bromide bridging ligands in contrast to chloride. The quantitative results of the present work confirm the speculation of Grinberg and Shagisultanova,[7] which was based on very fragmentary evidence, that bromide ligands were traded between *trans*-$Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$.

Sharp-Line Luminescence and Absorption Spectra of the Tetrachloroplatinate(II) Ion Doped in Single Crystals of Cesium Hexachlorozirconate(IV) at 4°K

BY HOWARD H. PATTERSON,*[1a] JOHN J. GODFREY,[1a] AND S. M. KHAN[1b]

The optical spectrum of the tetrachloroplatinate(II) ion in single crystals and as an impurity in Cs_2ZrCl_6 has been measured at 4°K. First, sharp-line luminescence has been observed between 19,450 and 23,190 cm^{-1} for the tetrachloroplatinate(II) ion in mixed crystals and assigned to the transition $\Gamma_5(^3B_{1g}) \rightarrow \Gamma_1(^1A_{1g})$. Most of the detailed vibronic structure can be assigned to odd vibrational modes of the $PtCl_4^{2-}$ complex in its ground electronic state. Franck–Condon analysis of the luminescence spectrum has shown that the Pt–Cl equilibrium distance in the $\Gamma_5(^3B_{1g})$ excited state is 0.16 Å greater than in the ground state. Second, the d–d transition $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_2(^1A_{2g})$ has been observed between 24,800 and 28,000 cm^{-1} with detailed vibronic structure. Finally, a crystal field analysis within the d^8 manifold fits the available experimental maxima data with an rms deviation of about 100 cm^{-1} for the parameters $F_2 = 1406$, $F_4 = 54$, $SO = 1013$, $\Delta_1 = 25,961$, $\Delta_2 = 41,821$, and $\Delta_3 = 33,184$ cm^{-1}.

Introduction

In order to eliminate metal–metal interactions present in pure single crystals we have grown single mixed crystals of the 5d^8 square-planar tetrachloroplatinate-(II) ion doped as an impurity in the host lattice cesium hexachlorozirconate(IV) and measured the optical spectrum of the mixed crystals at liquid helium temperature. Since the complex ions in the mixed crystal are isolated from each other and at 4°K reduced to their zero-point vibrational motion, sharply resolved spectra for some transitions can be obtained. The optical data can be analyzed to yield information about the vibrational modes of the excited electronic states and the proper assignment of these states.

Optical measurements for the $PtCl_4^{2-}$ complex until now have consisted of solution and crystal studies. Martin, Tucker, and Kassman[2] and Mortensen[3] have studied the polarized optical absorption spectrum of single K_2PtCl_4 crystals at liquid helium temperature and were able to assign the transition at 26,000 cm^{-1} as $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_2(^1A_{2g})$. McCaffery, Schatz, and Stephens[4] have studied the magnetic circular dichroism of a single K_2PtCl_4 crystal at 4°K. Their results strongly suggest that the transition observed at 30,000 cm^{-1} can be assigned as $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_5(^1E_g)$. Finally, Webb and Rossiello[5] have observed luminescence for K_2PtCl_4 at 77°K with a peak maximum at 12,700 cm^{-1} and a half-width of 2400 cm^{-1}.

Experimental Section

Single K_2PtCl_4 Crystals.—The K_2PtCl_4 used for this study was purchased from Alfa Inorganics, Inc. In a first attempt to grow large crystals of K_2PtCl_4, an acidified solution of the platinum complex was heated to 70° and then allowed to cool slowly back to room temperature. However, it was observed that upon heating the solution black particles began to form and upon cooling such a solution, a small-grained yellow precipitate could be obtained even if the volume of the solution was such that the orange-red K_2PtCl_4 should not precipitate. The yellow substance dissolved slowly in a high concentration of HCl. The black particles were suspected to be platinum metal and the yellow precipitate fitted the description of K_2PtCl_6. The reaction responsible for these products would be

$$2PtCl_4^{2-} \longrightarrow Pt + PtCl_6^{2-} + 2Cl^- \qquad (1)$$
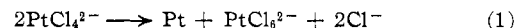
To prevent reaction 1 from occurring a different method for growing K_2PtCl_4 crystals was devised. A saturated solution of K_2PtCl_4 with a high concentration of KCl at room temperature was allowed to evaporate in a desiccator with concentrated H_2SO_4 as the drying agent. This method had a twofold advantage over the original method: (a) the condensation was performed without the addition of heat which seemed to hasten the disproportionation; (b) the excess chloride ion concentration decreased the amount of disproportionation. Using this method large crystals (1 × 1 × 4 mm) were harvested after 2 or 3 days.

Preparation of Cs_2PtCl_4–Cs_2ZrCl_6 Mixed Crystals.—The preparation of cesium hexachlorozirconate(IV) has been described in earlier publications.[6,7] The mixed crystals of Cs_2PtCl_4–Cs_2ZrCl_6 were prepared by placing a weighed amount of the platinum complex with Cs_2ZrCl_6 in an evacuated Vycor tube. The mole per cent of the platinum complex was 0.1–1.0%. The Vycor tube was dropped through a 24-in. vertical furnace at 800° in about 2 days' time. Large clear mixed crystals were obtained. Sections of the mixed crystals for optical studies were cleaved with a razor blade. It is known that the $ZrCl_6^{2-}$ complex does not absorb up to 45,000 cm^{-1};[6,8] therefore, the spectra reported here cannot be due to the host material.

Spectroscopic Measurements.—The crystals were mounted in an Air Products and Chemicals Inc. Model AC-3L Cryo-Tip. This instrument provided temperatures down to the liquid helium range using liquid nitrogen and gaseous hydrogen and helium. The temperature was measured with a chromel–constantan thermocouple.

The optical spectra were recorded with a McPherson 1-m

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