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Isotopic Exchange of Bromine in Aqueous System: cis-Dibromodiammineplatinum(II), Tetrabromoplatinate(II), Bromide

G. F. VANDEGRIFT, III, and D. S. MARTIN, Jr.
Ames Laboratory, USAEC and the Chemistry Dept., Iowa State University Ames, IA 50010, U.S.A.

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The aquation equilibria for cis-dibromodiammine-platinum(II) have been measured. For the first and second aquations at 25° C: $K_1 = 1.13$ mM. $\Delta H^\circ = 3.9 \pm .7$ kcal/mol, $K_2 = 0.042$ mM, $\Delta H^\circ = 10 \pm 3$ kcal/mol. Some isotopic exchange of ^{82}Br between c-$Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$ occurs without the formation of a free bromide ion and with a rate expression: Rate Exchange = $(k_{ac}' + k_{ac}''/[Br^-])[Pt(NH_3)_2Br_2][PtBr_4^{2-}]$. It has been shown that the presence of c-$Pt(NH_3)_2Br(H_2O)^+$ serves to catalyze the aquation of $PtBr_4^{2-}$, but that the catalysis step does not account for all the bromide dependent exchange.

Introduction

In a recent study of the *trans*-dibromodiammineplatinum(II)[1], it was found that the complex was capable of exchanging its bromide ligands without the formation of a bromide intermediate. This was another instance of "anomalous" ligand exchange processes[2] which require transition states dimeric in platinum complexes in contrast to the normal processes. For the normal processes the rate expression for the ligand replacement under the pseudo first order conditions of excess nucleophile is

$$\text{Rate} = [\text{Pt-complex}](k_s + k_y[Y]) \qquad (1)$$

where the square brackets designate molar concentrations, k_s is the rate constant for the replacement of the leaving ligand by solvent and k_y is the second order rate constant for the direct attack of the complex by the nucleophile, Y. Equation (1) applies when Y replaces the solvent ligand rapidly, and the solvation and the direct attack by Y have comparable rates. Excellent reviews of the normal processes for the platinum(II) complexes are available.[3,4]

In the present work the isotopic bromine exchange has been studied in the ternary exchange system: *cis*-dibromodiammineplatinum(II), tetrabromoplatinate(II), bromide. This system has revealed still another example of the "anomalous" ligand exchange. In addition, the exchange rate is slower than for the *trans* isomer and therefore provides a better characterization of the "anomalous" process. Previously, the bromine exchange has been studied for the two binary systems, $PtBr_4^{2-}$:Bromide[5] and *c*-$Pt(NH_3)_2Br_2$:Bromide.[6]

Experimental

Materials

The preparation of *cis*-$Pt(NH_3)_2Br_2$ was described by Gano *et al.*[6] and the preparation of $Rb_2PtBr_4 \cdot H_2O$ by Teggins *et al.*[5] $RbClO_4$ was purchased from the G. Frederick Smith Co. and was converted to the bromide by passage through a bed of Amberlite IRA 400 resin in the bromide form. Following its evaporation to dryness, the RbBr cake was ground and dried at 120° C for 15 hours. The $Hg_2(ClO_4)_2$ was prepared by the method described by Vogel.[7]

The Amberlite IRA 400 anion exchange resin, 20–50 mesh, was purchased from the Rohm and Haas Co. in the chloride form. It was converted to the nitrate form to be used for removing Br^- and $PtBr_4^{2-}$ from solutions of the *c*-$Pt(NH_3)_2Br_2$.

The radioactive ^{82}Br was prepared in the Ames Laboratory Research Reactor by the method described previously.[5]

The water used for the kinetics studies was distilled from alkaline permanganate.

Equipment

Absorption spectra in the visible and ultraviolet were recorded by a Cary Model 14 spectrophotometer which was equipped with a jacketed cell to provide temperature control.

A radiometer model SBR2c/ABU1c/TTT1C automatic recording titrator, with a 0.2500 ml ± (1μ + .07%) burette in conjunction with a glass indicator electrode and a saturated calomel reference electrode served for the titration of the acidic protons in aquo ligands of the complexes by standard base.

The radioactive bromide was counted by a scintillation spectrometer with a 3″ × 3″ well-type NaI(Tl) crystal, with a RIDL 400 channel analyzer.

Procedures

In the titration of the aquo ligands for the evaluation of equilibrium quotients, the solutions with the complex, the desired bromide concentration and enough $NaNO_3$ to give an ionic strength of $0.05M$ were aged at either 25.0° C or 35.0° C for two days in flasks which were wrapped with black opaque tape. Aliquots of these solutions, usually 10 ml, were transfered into the jacketed titration cells, thermostated by circulating water. The cell cover with the nitrogen gas inlet to provide flushing and the stirrer was set in place. Each titration was completed in 30 sec following the introduction of the first base. At least six titrations were performed for each solution. End points were determined from the inflection points on the recorder charts. The titer for blank, consisting of the same volume $NaNO_3$ solutions titrated to the end-point pH, was subtracted from each result. A few titrations at half the base introduction rate gave essentially the same titers.

The rate at which radiotracer ^{82}Br entered c-$Pt(NH_3)_2Br_2$ was determined both in the absence and in the presence of $PtBr_4^{2-}$. With $PtBr_4^{2-}$ the exchange was followed both for the cases when the $PtBr_4^{2-}$ was initially tagged or untagged. For example in the absence of $PtBr_4^{2-}$, the calculated quantities of c-$Pt(NH_3)_2Br_2$, KBr, and $NaNO_3$ were weighed into a 1000 ml volumetric flask which was then filled with distilled H_2O. The solution was stirred for 12–18 hours and permitted to equilibrate in the dark for 24–28 hours in a thermostated bath. The exchange was initiated by the addition of 50 μl of the NH_4Br tracer solution. At measured times 75 ml aliquots were withdrawn and subjected to the ion exchange replacement of anions according to the procedure of Gano *et al.*[6] The complexed bromide in the column eluate was removed by the boiling with NH_3, acidification with HNO_3 and precipitation as Hg_2Br_2. The specific activity was determined by counting and weighing the samples. The "infinity" specific activities were determined by recovering the total bromide from a small aliquot of the reaction solution.

For exchange of c-$Pt(NH_3)_2Br_2$ in the presence of untagged $PtBr_4^{2-}$ the above procedure was used except that $Rb_2PtBr_4 \cdot H_2O$ was weighed in with the other components. For the case where $PtBr_4^{2-}$ was to be tagged initially, a solution of $Rb_2PtBr_4 \cdot H_2O$, KBr, and $NaNO_3$ was prepared and divided into a 950 ml and a 50 ml portion. The solid c-$Pt(NH_3)_2Br_2$ was added to the larger portion and 50 μl of the NH_4Br radiotracer solution to the smaller. The exchange was initiated by mixing the solutions following the equilibration period.

For cases in which the entry of ^{82}Br into $PtBr_4^{2-}$ was to be measured, either with or without the c-$Pt(NH_3)_2Br_2$ in the solution, the $PtBr_4^{2-}$ was precipitated by tetraphenylarsonium ion which removes both $PtBr_4^{2-}$ and $PtBr_3(H_2O)^-$ cleanly from the solution.[5] The precipitates were then dried for later counting of the radioactivity. It was necessary to accomplish the filtration within 15 seconds to preclude exchange between the precipitates and free bromide. Infinity time samples were taken after 10 half lives. When the c-$Pt(NH_3)_2Br_2$ was untagged, the c-$Pt(NH_3)_2Br_2$ was added to solution initially. Because it dissolved slowly 12–18 hours were required. It was necessary to delay the infinity time samples until the slower exchanging $Pt(NH_3)_2Br_2$ had effectively reached its isotopic equilibrium. When the c-$Pt(NH_3)_2Br_2$ was initially tagged a 50 ml solution of c-$Pt(NH_3)_2Br_2$, KBr and $NaNO_3$ was first prepared. To a 1 ml fraction was added 50 μl of the radiotracer solution and to the remaining fraction was added the $Rb_2PtBr_4 \cdot H_2O$. Both fractions were allowed to equilibrate 3–4 days. The exchange was initiated by combining the fractions.

Results and Discussion

Aquation Equilibria for c-Pt(NH$_3$)$_2$Br$_2$

The equilibrium quotients which had been reported previously for c-$Pt(NH_3)_2Br_2$[6] were redetermined since the automatic titrator made possible much more accurate determinations. The method depends upon the feature that one proton from each H_2O-ligand can be titrated with an end point that lies between the pH of 8.5 and 9.5.

$$c\text{-}Pt(NH_3)_2Br_2 + H_2O \rightleftarrows c\text{-}Pt(NH_3)_2(H_2O)Br^+ + Br^-, K_1 \quad (2)$$

$$c\text{-}Pt(NH_3)_2(H_2O)Br^+ + H_2O \rightleftarrows c\text{-}Pt(NH_3)_2(H_2O)_2^{2+} + Br^-, K_2 \quad (3)$$

For a solution which is prepared from a M c-$Pt(NH_3)_2Br_2$ and b M Br^- and permitted to equilibrate with respect to reactions (2) and (3), the titer, T, is given by the solution of the cubic equation,[8]

$$T^3 + (2b + K_1)T^2 + (b^2 + K_1b + K_1K_2 - K_1a)T - (K_1ab + 2K_1K_2a) = 0 \quad (4)$$

The titration data for 25° and 35° C are included in Table I. The indicated values of K_1 and K_2 were determined by the non-linear least squares technique which has been described previously.[9] The values of K_1 agree moderately well with the values of Gano *et al.*[6] where the two equilibrium quotients were determined from two manual titrations only. However, the present values for K_2, which are determined with less precision than K_1, are only 50% as large as the earlier values. The difference in aquation behavior between the *cis* and *trans* isomers of $Pt(NH_3)_2Br_2$ is quite striking. The K_1 for the *trans* isomer is only 3% of the value for the *cis* compound. In addition values of $T/a > 1.0$ required substantial second aquation for the *cis* isomer. For the trans isomer no second aquation was detectible even when the pH was raised to 9.5. From that obser-

TABLE I. Titration Data for the Aquation Equilibrium Quotients of *cis*-$Pt(NH_3)_2Br_2$, K_1 and K_2 for the Ionic Strength 0.05. Each titer is the Average of Six Titrations.

Total Pt *a* m*M*	Bromide Added *b* m*M*	Equilibrium Titer *T* meq.	
		Obsvd.	Calcd.
	25° C		
1.500	0.00	0.883	0.894
1.500	2.00	.476	.483
1.500	5.00	.270	.269
1.500	10.00	.149	.152
1.500	20.00	.083	.080
1.500	30.00	.057	.055
1.500	40.00	.044	.041
1.500	50.00	.035	.033
1.200	0.00	.761	.768
0.900	0.00	.636	.629
.750	0.00	.558	.553
.600	0.00	.480	.470
.375	0.00	.342	.332
.150	0.00	.178	.164
K_1 = 1.13 ± .03 m*M*		K_2 = 4.2 ± 6 × 10^{-2} m*M*	
	35° C		
1.50	0.00	0.955	0.976
1.20	0.00	0.827	0.838
0.90	0.00	0.684	0.686
0.75	0.00	0.603	0.602
0.60	0.00	0.520	0.513
0.45	0.00	0.413	0.415
0.30	0.00	0.311	0.3055
0.15	0.00	0.187	0.179
1.50	1.50	0.630	0.629
1.50	3.00	0.462	0.449
1.50	6.00	0.267	0.280
1.50	9.00	0.204	0.201
1.50	15.00	0.139	0.128
K_1 = 1.40 ± .03 m*M* $\Delta H°_1$ = 3.9 ± .7 kcal/mol		K_2 = 7.5 ± .6 × 10^{-2} m*M* $\Delta H°_2$ = 10 ± 3 kcal/mol	

vation the upper limit of K_2 for the *trans* isomer has been estimated at $10^{-7}M$.

Elding[10] has reported values of the aquation rate constants for $PtBr_4^{2-}$ from careful spectrophotometric measurements. He noted at ionic strength of 0.5*M* that at least two weeks were required to attain the equilibrium with respect to the five possible complexes of the aquo-bromo system. From his equilibrium quotients of 1.8 m*M* and 2.6 m*M* for 25° and 35° C respectively, we have estimated quotients of 2.6 m*M* and 3.6 m*M* at $\mu = 0.05M$ from the expected dependence of activity coefficients upon ionic strength. We have confirmed these values by the titration technique with sufficient bromide present that the subsequent aquations did not influence the titer substantially.

Isotopic Exchange

The isotopic exchange was considered to occur between the three components; *c*-$Pt(NH_3)_2Br_2$, $PtBr_4^{2-}$ and Br^-. Both of the complexes, of course, undergo the aquation reactions. High bromide concentrations decrease the equilibrium concentrations of the aquo complexes. At a bromide concentration of 10 m*M*, the *c*-$Pt(NH_3)_2Br_2$ concentration has been reduced by only *ca.* 10% and the $PtBr_4^{2-}$ concentration has been reduced by 25% by aquation. The non-aquated complexes were therefore still the dominant species. Although, as will be seen below, the aquo species participate in the exchange processes, very great complications in the treatment can be avoided by employing the approximation that aquo complexes possess only a negligible fraction of the exchanging bromide. The exchange processes in a steady-state chemical system are established by the three exchange rates of the system depicted in Figure 1. Two independent differential equations are required to describe isotopic exchange in the three component system of Figure 1.

$$du_a/dt = R_{ab}\,(S_b - S_a) + R_{ac}\,(S_c - S_a), \tag{5}$$

$$du_c/dt = R_{bc}\,(S_b - S_c) + R_{ac}\,(S_a - S_c), \tag{6}$$

where the subscripts refer to the components indicated in Figure 1 and u = concentration of radioactivity (^{82}Br) in the indicated component, cts min^{-1} l^{-1}. S = the specific activities of bromide in the components, cts min^{-1} mol^{-1}.

The specific activities correspond to the quantities:

$$S_a = u_a/2a\,;\, S_c = u_c/4c\,;\, S_b = (I - u_c - u_a)/b \tag{7}$$

where I is the total concentration of ^{82}Br, cts min^{-1} l^{-1}.

In the isotope exchange experiments the introduction of ^{82}Br into one of the complexes, either *c*-Pt $(NH_3)_2Br_2$ or $PtBr_4^{2-}$, which originally contained no ^{82}Br, was followed as a function of time. The conditions in the experiments for the introduction of ^{82}Br into *c*-$Pt(NH_3)_2Br_2$ are listed in Table II; and for the introduction into $PtBr_4^{2-}$ the conditions of the experiments are in Table III.

A fraction of exchange for *c*-$Pt(NH_3)_2Br_2$, F_a, can be defined,

$$F_a = (u_a - u_{a,0})/(u_{a,\infty} - u_{a,0})\,; \tag{8}$$

and for $PtBr_4^{2-}$

$$F_c = (u_c - u_{c,0})/(u_{c,\infty} - u_{c,0}), \tag{9}$$

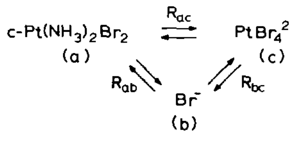

Figure 1. Scheme for exchange in the three-component system.

TABLE II. Isotopic Exchange Experiments for the Introduction of ^{82}Br into c-$Pt(NH_3)_2Br_2$. Ionic Strength = 0.050 *M*.

C-$Pt(NH_3)_2Br_2$ *a* m*M*	Br^- *b* m*M*	$PtBr_4^{2-}$ *c* m*M*	$S_c°$	Time of Half-Exchange Obsd–min	Time of Half-Exchange Calcd–min	R_{ab} ($10^{-8}Ms^{-1}$)	R_{ac} ($10^{-8}Ms^{-1}$)
				25° C			
0.75	30	0	–	510	–	3.2	–
0.75	30	3	0	240	289	3.2	5.7
1.0	30	0	–	478	–	4.5	–
1.0	30	3	0	254	278	4.5	7.7
1.5	2	0	–	265	–	5.4	–
1.5	2	3	$S_b°$	31	31	5.4	76.4
1.5	10	0	–	–	375	6.0	–
1.5	10	3	$S_b°$	89	89	6.0	27.5
1.5	20	0	–	420	–	7.0	–
1.5	20	3	0	208	215	7.0	15.7
1.5	20	3	$S_b°$	141	138	7.0	15.7
1.5	30	0	–	436	–	7.2	–
1.5	30	0.2	$S_b°$	337	391	7.2	0.8
1.5	30	1.0	0	387	352	7.2	3.8
1.5	30	1.0	$S_b°$	318	287	7.2	3.8
1.5	30	1.5	0	340	324	7.2	5.8
1.5	30	2.0	$S_b°$	213	215	7.2	7.7
1.5	30	2.0	0	304	300	7.2	7.7
1.5	30	2.5	0	286	281	7.2	9.6
1.5	30	3.0	$S_b°$	171	172	7.2	11.5
1.5	30	3.0	0	240	264	7.2	11.5
1.5	30	4.0	$S_b°$	134	144	7.2,	15.3
1.5	30	4.0	0	219	236	7.2	15.3
1.5	30	5.0	$S_b°$	130	124	7.2	19.0
1.5	30	6.0	$S_b°$	105	108	7.2	22.8
1.5	41	0	–	441	–	7.2	–
1.5	41	3	$S_b°$	199	200	7.2	9.1
2.0	30	0	–	471	–	8.5	–
2.0	30	3	0	264	279	8.5	15.3
				35° C			
1.5	20	0	–	137	–	21.3	
1.5	20	3.0	$S_b°$	45	46	21.3	45.7
1.5	30	0	–	145	–	21.8	
1.5	30	1	$S_b°$	102	97	21.8	10.8
1.5	30	2	$S_b°$	71	73	21.8	21.5
1.5	30	3	$S_b°$	58	59	21.8	32.2
1.5	41	0	–	144	–	22.3	–
1.5	41	3	$S_b°$	69	69	22.3	24.8

where the subscripts, 0 and ∞ imply zero and infinity time quantities.

Because of the nature of the system the values of *F* are not restricted to values between 0 and 1 and may in certain circumstances be greater than 1. However, for the conditions studied it was found that the generated curves $\ln(1-F_a)$ or $\ln(1-F_c)$ were nearly linear for times somewhat greater than that required for $(1-F)$ to fall to 0.5. It was expedient initially to fit the experimental points to a straight line by a weighted linear least squares procedure.

A typical exchange reaction for *c*-$Pt(NH_3)_2Br_2$ is shown in Figure 2. The experimental times of half-exchange listed in Table II were calculated from the slopes of these least squares lines. For the system indicated in Figure 1 the rates R_{ab} and R_{bc}, were expressed as

TABLE III. Isotopic Exchange Experiments for Introduction of ^{82}Br into $PtBr_4^{2-}$. 25° C. Ionic Strength = 0.050 *M*.

$PtBr_4^{2-}$ c m*M*	Br^- b m*M*	*Cis*-$Pt(NH_3)_2Br_2$ a m*M*	S_a	Time of Half Exchange Obsd–min	Calcd–min	R_{bc} ($10^{-8}M\ s^{-1}$)	R_{ac} ($10^{-8}M\ s^{-1}$)
3.0	20	0	–	112	–	77.4	–
3.0	20	1.5	0	104	102	77.4	15.7
3.0	30	0	–	154	–	64.5	–
3.0	30	1.5	S_b^0	131	134	64.5	11.2
3.0	30	1.5	0	140	145	64.5	11.2
4.0	30	0	–	127	–	95.1	–
4.0	30	1.5	0	136	134	95.1	15.3

$$R_{ab} = R_{ab}^0 + R_{ab}' \tag{10}$$

$$R_{bc} = R_{bc}^0 + R_{bc}' \tag{11}$$

where the zero superscript was taken to indicate the value of the exchange rate in the absence of the other complex.

The exchange experiments in Table II for which *c* was zero provided the rates, R_{ab}^0. These experiments were considered, of course, to involve two component systems for which the functions $(1-F_a)$ were true exponentials and the rate of exchange, R_{ab}^0 was given by the usual expression for exchange rate

$$R_{ab}^0 = \frac{(\ln 2)\, 2ab}{(2a+b)\,\tau_{1/2}} \tag{12}$$

where $\tau_{1/2}$ is the half-life of the exponential function. The half times for the experiments in the binary *c*-$Pt(NH_3)_2Br_2$: Br^- system generally agreed very satisfactorily with the earlier data.[6] For two experiments in which deviations from the earlier half-lives were greater than 5%, the experiments were repeated to check the results. The binary exchange data for $PtBr_4^{2-}$: Br^- could not be compared directly with the earlier results[5] since the ionic strength was considerably different (the lower ionic strength in the present experiments was required for effective ion exchange separation).

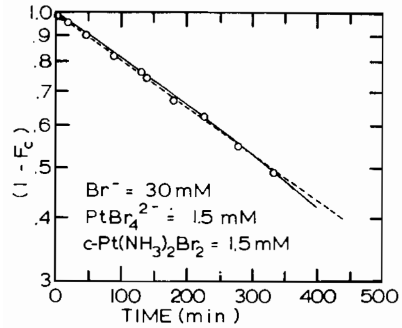

Figure 2. Typical exchange experiment with the $PtBr_4^{2-}$ untagged ($S_c^0 = 0$) 25° C and $\mu = 0.050M$. Dashed line is linear least squares fit and the solid curve is the Runge–Kutta calculation. Time of half-exchange = 340 min for the least squares fit and 324 min for the Runge–Kutta Fit.

In the exchange of *c*-$Pt(NH_3)_2Br_2$ in the presence of $PtBr_4^{2-}$ which had already equilibrated with the tagged Br^-, the S_c^0 and S_b^0 of equation 5 are equal. Furthermore since the bromide in *c*-$Pt(NH_3)_2Br_2$ constitutes such a small fraction of the total bromide, the values of S_c and S_b are substantially constant. The rate expression approaches closely the expression for exchange in a binary system with the tagged component in considerable excess. From the half-times of the plots of $\ln(1-F_a)$ *vs* time were estimated values for $R_{ab} + R_{ac}$ by the equation

$$(R_{ab} + R_{ac}) = (\ln 2)\, 2a/\tau_{1/2}. \tag{13}$$

For the experiments in which the $PtBr_4^{2-}$ was tagged initially an S_b^0 appears in the columns for the S_c^0's in Table II. It can be seen that the observed half-life was considerably shortened in the presence of tagged $PtBr_4^{2-}$ and this feature indicates substantial values for $R_{ab}' + R_{ac}$.

A process, characterized by R_{ab}', can be considered a catalysis of the exchange between *c*-$Pt(NH_3)_2Br_2$ and Br^- by the $PtBr_4^{2-}$. On the other hand, the process characterized by R_{ac} represents a trading of bromide ligands directly between *c*-$Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$ without the formation of a Br^- intermediate. The contribution of R_{ab}' can be inferred from the initial exchange rate for *c*-$Pt(NH_3)_2Br_2$ when the $PtBr_4^{2-}$ was untagged. At that time, both S_c and S_a in equation 5 are zero and there results:

$$R_{ab} = [-d\ln(1-F_a)/dt]\, 2ab/(2a+b+4c) \tag{14}$$

Initial values for R_{ab} were calculated from the slopes of the linear plots of $\ln(1-F_a)$ *vs* time. It can be seen from the data in Table II that when S_c^0 equalled zero the exchanged half-time was considerably longer than when $S_c^0 = S_b^0$ for comparable concentration conditions. This initial treatment indicated an increase in R_{ab} of approximately 20% by the addition 4 m*M* $PtBr_4^{2-}$ (untagged). The result indicated that R_{ab}' was much smaller than R_{ac} in the solutions with the initially tagged $PtBr_4^{2-}$. It was also apparent from

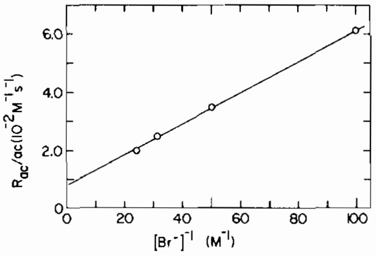

Figure 3. The bromide dependence of the rate for exchange of bromide ligands between c-$Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$. 25°C and $\mu = 0.050 M$. From the intercept, $k_{ac}' = 8.0 \times 10^{-3} M^{-1}s^{-1}$ and from the slope $k_{ac}'' = 5.31 \times 10^{-4}s^{-1}$.

these indicated tentative rates that R_{ac}, for constant bromide concentration was proportional to the concentration of c-$Pt(NH_3)Br_2$ and to the concentration of $PtBr_4^{2-}$. However the plot in Figure 3 shows how the rate decreases as the concentration, $[Br^-]$, increased. Therefore, the rates were fitted to an expression of the form.

$$R_{ac} = [c\text{-}Pt(NH_3)_2Br_2][PtBr_4^{2-}](k_{ac}' + k_{ac}''/[Br^-]) \quad (15)$$

From a set of three exchange rates, R_{ac}, R_{ab}, R_{bc} the pair of differential rate equations, (5) and (6) could be solved numerically by the Runge–Kutta technique.[11] The plot of $\ln(1-F_c)$ *vs* time was discernably curved for the experiments in which $PtBr_4^{2-}$ was initially untagged, a feature which is illustrated in Figure 2. In this refinement the indicated value of R_{ab}' was negligible in comparison to R_{ab}^0. The value obtained in the preliminary treatment may have resulted from the use of a linear plots for $\log(1-F)$ rather than the true slopes of the curves at zero time. The values of k_{ac}' and k_{ac}'' were therefore refined to minimize the per cent deviations of the experimental and the calculated times of half-exchange. The final calculated times of half-exchange are included in Table II which also contains the values of R_{ab} and R_{ac} calculated from the adjusted rate constants. The rate constants are listed in Table IV.

Only a few exchange experiments for $PtBr_4^{2-}$ are recorded in Table III. The value of R_{ac} was taken from the results of the exchange experiments of c-$Pt(NH_3)_2Br_2$ at the same conditions. It can be seen that the indicated value of R_{bc}^0 is more than five times larger than R_{ac}. Hence the half time of the exchange for $PtBr_4^{2-}$ with Br^- is changed only slightly by the addition of the c-$Pt(NH_3)_2Br_2$. The agreement between the calculated and observed times of half-exchange indicate that the catalysis of the exchange between $PtBr_4^{2-}$ and Br^-, *i.e.*, R_{bc}', is negligible. The magnitude of R_{ac} would be increased by increasing the concentration of c-$Pt(NH_3)_2Br_2$ but its concentration is limited by its solubility. Also a decrease in bromide would increase R_{ac}; however, there would also be a large increase in R_{ab}^0 as well.[5]

TABLE IV. Rate Constants and Kinetic Parameters. Ionic Strength = 0.050 *M*.

	k_{ac}' $(10^{-3}\ M^{-1}\ s^{-1})$	k_{ac}'' $(10^{-4}\ s^{-1})$
25°C	8.0 ± 1.2	5.3 ± .1
35°C	13 ± 1	14.0 ± .1
ΔH^*	8.3 ± 1.2	17.8 ± .3
ΔS^*	–40 ± 5	–14 ± 1

It is proposed that the bromide trading between the c-$Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$ species, *viz.* the process characterized by k_{ac}' in equation 5 occurs by the mechanism in which a double bromide-bridged transition complex is formed as shown in Figure 4. This first step shown in 4A is an attack by the bromide ligand of one complex along the axial position of the other complex to form a weak bridging bond. Rotation of the complexes will permit the formation of the two weak unsymmetric bridges in 4B. Symmetric bridges are formed in a transition state when the two ligands *trans* to the bridges move according to the arrows to form 4C. The activation enthalpy of *ca.* 8.3 kcal/mol for this process is considerably lower than that for most direct halide ligand replacement processes of platinum (II) complexes. The moderately large negative entropy of activation is reasonable for such a bimolecular reaction with fairly severe steric requirements.

The major portion of the bromide trading between the complex systems was accomplished by the process which was inversely proportional to the bromide concentration, *i.e.* characterized by k_{ac}'' in equation 15. This bromide dependence suggests that the transition state is attained by the reaction of one of the complexes with the monoaquo species of the other complex. A

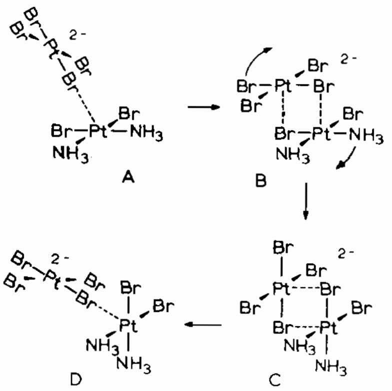

Figure 4. Possible mechanism for the trading of bromide ligands between c-$Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$.

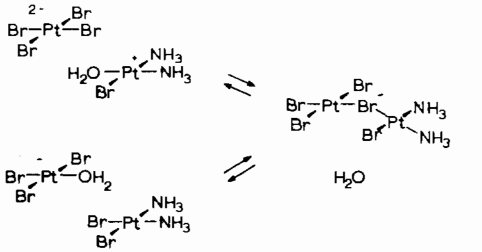

Figure 5. Possible mechanism for the catalysis of the aquation processes.

possibility exists for the displacement of the aquo ligand to the solvent in the formation of a single bromide bridge as is shown in Figure 5. The bridging bromide could then be displaced to either platinum by an aquo group which enters the coordination sphere of the other platinum. However, if exchange occurred by this process the result would be an enhancement or catalysis of the rate of aquation of complexes. A consideration of the magnitude of the rate constant, k_{ac}'' indicated that such catalysis would measurablely alter the aquation rate for $PtBr_4^{2-}$ and an experiment was undertaken to detect such catalysis.

A solution, prepared from 1.5 mmol/l of c-$Pt(NH_3)_2Br_2$ with $\mu = 0.05M$, was allowed to equilibrate at 25° C. From the values of K_1 and K_2 the following concentration of species for equilibrium were calculated to be: c-$Pt(NH_3)_2Br_2$ = 0.65 mM, c-$Pt(NH_3)_2Br(H_2O)^+$ = 0.82 mM, c-$Pt(NH_3)_2(H_2O)_2^{2+}$ = 0.038 mM, Br^- = 0.89 mM. To this solution was added 0.1 mmol/l of Rb_2PtBr_4. Following a procedure worked out by Elding[10] the aquation of the $PtBr_4^{2-}$ was observed by measuring the absorbance of the solution at 268 nm as a function of time. At this wavelength the molar absorptivity of c-$Pt(NH_3)_2Br_2$ is *ca.* 150 $cm^{-1} M^{-1}$ while for $PtBr_4^{2-}$ there is the maximum of a charge transfer band with a molar absorptivity of 10,000 $cm^{-1}M^{-1}$. The concentrations of bromide and of the species based on c-$Pt(NH_3)_2Br_2$ were not changed substantially by the aquation of the $PtBr_4^{2-}$. Since there is a moderate excess of Br^-, in the absence of catalysis, the $PtBr_4^{2-}$ is expected to approach equilibrium with respect to the formation of $PtBr_3(H_2O)^-$ by a first order process for which k_{obs} is given by the equation

$$k_{obs} = k_{c,1} + k_{c,-1}[Br^-] \tag{16}$$

where $k_{c,1}$ and $k_{c,-1}$ are the rate constants for the reaction,

$$PtBr_4^{2-} + H_2O \underset{k_{c,-1}}{\overset{k_{c,1}}{\rightleftharpoons}} PtBr_3(H_2O)^- + Br^-. \tag{17}$$

Values of $\log(A_t - A_{t+\tau})$ *vs* time (a Guggenheim plot) are shown in Figure 6 where k_{obs} was found to be

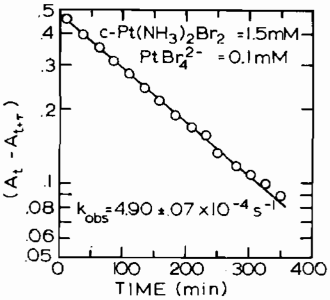

Figure 6. Guggenheim plot for the aquation of $PtBr_4^{2-}$ in the presence of c-$Pt(NH_3)_2Br_2$. The absorbances were recorded at 268 nm. 25° C $\mu = 0.050M$.

$4.90 \times 10^{-4} s^{-1}$. From a value of $2.2 \times 10^{-4} s^{-1}$ for $k_{c,1}$ at 25° C and the value of $2.6 \times 10^{-3} M$ for $K_{c,1}$ the calculated value of k_{obs} without catalysis would be only $3.0 \times 10^{-4} s^{-1}$. It appears therefore that in the presence of c-$Pt(NH_3)_2Br_2$ and c-$Pt(NH_3)_2Br(H_2O)^+$ there is some catalysis. The value of k_{obs} can now be computed if the process characterized by k_{ac}'' contributes to the aquation rates in accordance with the process shown in Figure 5. Under steady state conditions the rate of exchange by this process is given by the equation

$$\begin{aligned} k_{ac}''/[Br^-] &= k_2[Pt(NH_3)_2Br(H_2O)^+][PtBr_4^{2-}] \\ &= k_{-2}[Pt(NH_3)_2Br_2][PtBr_3(H_2O)^-] \end{aligned} \tag{18}$$

where $k_2 = k_{ac}''/K_{a,1} = 0.47 M^{-1}s^{-1}$ at 25° C, $k_{-2} = k_{ac}''/K_{c,1} = 0.20 M^{-1}s^{-1}$ at 25° C, $K_{a,1}$ and $K_{c,1}$ are the first aquation equilibrium quotients for c-$Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$ respectively.

The expected value of k_{obs} is then given by the expression

$$\begin{aligned} k_{obs} = k_{c,1} &+ k_2[c\text{-}Pt(NH_3)_2Br(H_2O)^+] \\ &+ k_{c,-1}[Br^-] + k_{-2}[c\text{-}Pt(NH_3)_2Br_2] \end{aligned} \tag{19}$$

The value calculated for the experimental conditions of Figure 6 is $7.9 \times 10^{-4} s^{-1}$. Since the calculated value is significantly larger than the observed value of $4.9 \times 10^{-4} s^{-1}$ it appears that a process leading to catalysis of aquation, such as Figure 6, accounts for only a fraction, about 40%, of the process characterized by k_{ab}''. The remaining portion of the reaction might occur *via* double bromide bridged intermediate of the type illustrated in Figure 4, but in which one of the nonbridging bromide ligands had been replaced by an aquo ligand.

The involvement of dimeric transition states to provide either an exchange of ligands between two complex species or the catalysis of solvation appears to be a fairly common process in the bromide systems of platinum(II). The mechanism proposed in Figure 4 is essentially the same as that also proposed for the t-Pt

$(NH_3)_2Br_2$–$PtBr_4^{2-}$. However, because of the slower rates associated with the *cis*-complex a much better characterization of the exchange is possible to provide the resulution into the bromide independent and the bromide dependent components. The involvement of the dimeric transition states for the bromide complexes may reflect the greater stability of bromide bridges in comparison to chloride for the platinum(II) complexes. In addition, the catalyst of the aquation of $PtBr_4^{2-}$ has indicated that at least two mechanisms are involved in the bromide dependent term. It is also interesting to recall the speculation of Grinberg and Shagisultanova.[12] They had noted that when the *c*- and *t*-$Pt(NH_3)_2Br_2$ were in solutions of K_2PtBr_4 there was a more rapid exchange of bromide than in K_2PtBr_4 exchange with Br^-. They concluded therefore that there must be a trading of ligands. However, only fragmentary data was presented and apparently the concentration of free bromide was not controlled in their experiments.

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