point clockwise *as shown* while the chelate rings spiral to the left. On this basis it is reasonable that the configurational and vicinal effects are of opposite sign in the low-frequency band region, partially cancelling one another to give two weak peaks of opposite sign. The resultant optical activity in the visible region is so weak that the effect of the contribution from the stronger ultraviolet transitions causes the ORD curve of β-[Co(L-ala)$_3$] to be entirely negative in the visible region.

The methyl groups are axial for the β′ isomer and point in the same direction as shown (horizontal component clockwise) as the spiral of the chelate rings. The configurational and vicinal contributions are in the same direction and add to give a single, more intense peak than for β.

The peaks for the vicinal effect are displaced so much to higher frequencies compared to the configurational effect that it is apparent that the dominant components are not the same for the two effects. This was also true for the [Co(en)$_2$am]I$_2$ compounds. For the α and α′ compounds the dominant CD peak overshadows the others, but from the vicinal effect the corresponding peak can be seen to be the center peak (of three) of comparable intensity to one of higher frequency (21,400 cm.$^{-1}$).

The methyl groups are equatorial for α′, corresponding to β with one chelate ring reversed. Two of the methyl groups point in the opposite direction (as shown) to the left spiral and one points in the same direction. Thus the vicinal effect is smaller than for β and β′. The vicinal effect curve can be seen to have the effect of lowering the maximum and broadening the resultant (experimental) curve for α′. The methyl groups are axial for α with the horizontal component in the same direction as shown (clockwise) for only two of the groups. The third methyl group points down and counterclockwise. The sign combination of peaks for the vicinal effect when added to the configurational effect curve gives the sharp positive peak flanked by the weak negative peak of the experimental curve for α (Figure 1).

It is apparent that for complexes with three chelate rings the contribution to the optical activity from the configurational effect is larger than that from the vicinal effect. The vicinal effect is reduced when the substituents are oriented in such a way as to cancel partially their effects, as for the α and α′ isomers. The two effects contribute to different extents to the intensities of different CD components in the low-frequency region and the vicinal effect has little effect in the higher frequency band region.

The lower solubility of β-[Co(ala)$_3$] compared to α-[Co(ala)$_3$] is not so surprising since the molecules of the β isomer might be expected to interact strongly through intramolecular hydrogen bonding which would be possible if the molecules were stacked directly above one another. Models do not reveal any significant differences in the opportunities for hydrogen bonding to water. The great increases in water solubilities caused by changing the methyls from equatorial positions (α′ and β) to axial positions (α and β′) is surprising. The difference is especially great for β and β′. Framework molecular models show that the axial methyl groups for the β′ isomer project up far enough so that they might interfere with intramolecular hydrogen bonding and thus increase solubility.

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Studies on the Interconversion of *trans*-Dichlorotetraammineplatinum(IV) and *trans*-Dibromotetraamineplatinum(IV) Cations

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The reactions of bromide ion with *trans*-$Pt(NH_3)_4Cl_2^{2+}$ and *trans*-$Pt(NH_3)_4ClBr^{2+}$ and the reverse reactions of chloride with *trans*-$Pt(NH_3)_4ClBr^{2+}$ and *trans*-$Pt(NH_3)_4Br_2^{2+}$ exhibit a first-order rate dependence in the reactant platinum(IV) complex, in the entering halide ion, and in $Pt(NH_3)_4^{2+}$. These rate data are consistent with a mechanism involving a bridged activated complex, Pt–X–Pt. Rate constants and activation parameters for the four reactions were measured. Reactions in which a bromine atom is *trans* to the leaving halide are much more rapid than those in which the *trans* ligand is chloride. Equilibrium constants for the reactions were evaluated from the kinetic data and from independent spectrophotometric studies.

Introduction

A mechanism involving a bridged activated complex is consistent with the rate data for several substitution reactions of complex cations such as *trans*-$Pt(NH_3)_4X_2^{2+}$ and *trans*-$Pt(NH_2CH_2CH_2NH_2)_2X_2^{2+}$.[1,2] All reactions for which kinetic data are available show third-order

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[1] W. R. Mason and R. C. Johnson, *Inorg. Chem.*, **4**, 1258 (1965).

[2] F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 35 (1961).

kinetics, first-order in platinum(IV) complex, entering group, and a platinum(II) catalyst. The mechanism as proposed by Basolo and Pearson and applied to chloride exchange in *trans*-$Pt(NH_3)_4Cl_2^{2+}$ is outlined in eq. 1–3. (Four ammonias lying in the plane with each platinum atom are omitted.) This mechanism involves a two-

$$Pt^{2+} + {}^*Cl^- \underset{}{\overset{\text{fast}}{\rightleftharpoons}} Pt\text{–}{}^*Cl^+ \tag{1}$$

$$Cl\text{–}Pt\text{–}Cl^{2+} + Pt\text{–}{}^*Cl^+ \rightleftharpoons Cl\text{–}Pt\text{–}Cl\text{–}Pt\text{–}{}^*Cl^{3+} \tag{2}$$

$$Cl\text{–}Pt\text{–}Cl\text{–}Pt\text{–}{}^*Cl^{3+} \rightleftharpoons Cl\text{–}Pt^+ + Cl\text{–}Pt\text{–}{}^*Cl^{2+} \tag{3}$$

electron oxidation–reduction process. The details of this mechanism are of interest, since it seems probable that they will shed light on the mechanisms of oxidation–reduction and substitution reactions for other elements which exhibit two oxidation states, such as 0, 2^+; 1^+, 3^+; etc. A substitution reaction of Rh(III) has been reported to proceed by a similar mechanism in which a planar Rh(I) catalyst was effective.[3] The platinum systems are conveniently studied because both the Pt(IV) and Pt(II) complexes are inert, because a variety of such compounds are available, and because the reaction rates are suitable for traditional kinetic procedures.

This article describes the kinetic and equilibrium behavior of reactions 4 and 5. These reactions were

$$trans\text{-}Pt(NH_3)_4Cl_2^{2+} + Br^- \rightleftharpoons trans\text{-}Pt(NH_3)_4ClBr^{2+} + Cl^- \tag{4}$$

$$trans\text{-}Pt(NH_3)_4ClBr^{2+} + Br^- \rightleftharpoons trans\text{-}Pt(NH_3)_4Br_2^{2+} + Cl^- \tag{5}$$

chosen as a starting point in an extended study on the effects of the nature of the platinum(IV) complex, the platinum(II) complex, and the entering group on the rates and mechanisms of substitution reactions of platinum(IV) complexes.

Experimental

Materials.—*trans*-Dichlorotetraammineplatinum(IV) chloride and *trans*-$Pt(NH_3)_4Br_2Br_2$ were prepared by adding chlorine or bromine to solutions of $Pt(NH_3)_4Cl_2$ in the appropriate hydrohalic acid.[4] *trans*-Chlorobromotetraammineplatinum(IV) chloride was prepared by adding concentrated HCl to a hot aqueous solution of *trans*-$Pt(NH_3)_4Br_2Br_2$.[4] Nitrate salts of these compounds were prepared by treatment with stoichiometric amounts of $AgNO_3$. Tetraammineplatinum(II) chloride was prepared from K_2PtCl_4 by a published procedure.[5] The perchlorate salt was prepared by adding cold 72% $HClO_4$ to a cold concentrated solution of $Pt(NH_3)_4Cl_2$. All compounds were characterized by their ultraviolet spectra and platinum and halide analyses. Concentrations of $Pt(NH_3)_4(ClO_4)_2$ solutions were determined by titration with Ce(IV) in H_2SO_4 using chloride ion as a catalyst. Solutions of $NaClO_4$ were prepared from reagent Na_2CO_3 and $HClO_4$.

Kinetic Measurements.—All kinetic data were taken by recording absorbance *vs.* time on a Cary Model 14 spectrophotometer equipped with thermostated cell holders. The temperature of the reaction mixtures was controlled within ±0.1°. All platinum(IV) solutions were prepared in dilute $HClO_4$ and used the same day to eliminate the possibility of appreciable hydrolysis. No precautions were taken to exclude light. Infinite time spectra of all kinetic runs were identical with those of the expected reaction products.

The reverse of reaction 5 was followed at the 234 mμ absorbance maximum for $Pt(NH_3)_4Br_2^{2+}$ (ϵ 4.2×10^4, ϵ for $Pt(NH_3)_4ClBr^{2+}$ 2.5×10^4). The introduction of a second chloride is too slow to cause interference when the introduction of the first proceeds at a measurably slow rate. The reverse of reaction 4 was followed at 288 mμ, an absorbance maximum for *trans*-$Pt(NH_3)_4ClBr^{2+}$ (ϵ 600, ϵ for $Pt(NH_3)_4Cl_2^{2+}$ 150). The starting material for this reaction was *trans*-$Pt(NH_3)_4Br_2(NO_3)_2$, but under suitable conditions its conversion to *trans*-$Pt(NH_3)_4ClBr^{2+}$ is complete on mixing.

Reaction 4 was followed at 295 mμ, an isosbestic point for *trans*-$Pt(NH_3)_4Br_2^{2+}$ and *trans*-$Pt(NH_3)_4BrCl^{2+}$ (ϵ 580, ϵ for $Pt(NH_3)_4Cl_2^{2+}$ 110). This procedure was necessary because reaction 5 is more rapid than reaction 4. Reaction 5 was studied at 234 mμ. The starting material was *trans*-$Pt(NH_3)_4ClBrCl_2$.

In all kinetic runs $[X^-]/[Pt(IV) > 40$; therefore, pseudo-first-order kinetics were observed. First-order rate constants were calculated from ten-point Guggenheim plots[6] using a least-squares technique. Linear plots for data covering at least three half-lives were obtained in all runs. Third-order rate constants were calculated by dividing the pseudo-first-order constants by the $Pt(NH_3)_4^{2+}$ and halide concentrations. In data for reaction 5 a $[Pt(NH_3)_4^{2+}]$-independent rate was found by plotting $k_{obsd}/[Br^-]$ *vs.* $[Pt(NH_3)_4^{2+}]$. The slope of the resulting line was taken as the third-order rate constant. The intercept was the second-order rate constant for the $Pt(NH_3)_4^{2+}$-independent reaction.

The ionic strength of all reaction mixtures was adjusted to 0.20 *M* by addition of the requisite amount of 0.80 *M* $NaClO_4$ solution.

Equilibrium Studies.—The method described by Poë was used in these studies.[7] Solutions of 1.00 *M* NaCl and 1.00 *M* NaBr and a solution of *trans*-$Pt(NH_3)_4Br_2Br_2$ in dilute $HClO_4$ were used to prepare equilibrium solutions. The platinum(IV) concentration in the resulting solutions was 6.67×10^{-4} *M*; $[H^+]$ was 5.0×10^{-3} *M* and $[Cl^-] + [Br^-]$ was 0.200 *M*. The solutions were equilibrated at 25.0 ± 0.1° for 1 week. Measurements performed on samples after 4 days were identical with those taken after 7 days. A solution of *trans*-$Pt(NH_3)_4Br_2Br_2$ in 0.20 *M* NaBr and a solution prepared using *trans*-$Pt(NH_3)_4Cl_2Cl_2$ in 0.200 *M* NaBr had spectra in which the absorbances agreed within 2% after equilibration.

Absorbance measurements were made at 300 and 320 mμ using a Beckman DU spectrophotometer equipped with a Gilford optical density converter. The molar absorptivities of *trans*-$Pt(NH_3)_4Cl_2^{2+}$ and *trans*-$Pt(NH_3)_4Br_2^{2+}$ were obtained from spectra of pure compounds. The absorbance of *trans*-$Pt(NH_3)_4Br_2^{2+}$ is dependent on $[Br^-]$; therefore absorptivities of this ion were determined as a function of $[Br^-]$ in solutions containing $[Br^-] + [ClO_4^-] = 0.20$ *M*. The molar absorptivity of *trans*-$Pt(NH_3)_4ClBr^{2+}$ at 300 mμ was determined by following spectrophotometrically the reaction of *trans*-$Pt(NH_3)_4Br_2^{2+}$ with chloride. Since the rate of this reaction and the molar absorptivity of $Pt(NH_3)_4Br_2^{2+}$ are known, the molar absorptivity of the product *trans*-$Pt(NH_3)_4ClBr^{2+}$ could be calculated at points during the reaction and at the end. Allowance was made for the almost negligible amount of *trans*-$Pt(NH_3)_4Cl_2^{2+}$ formed. This procedure was not followed at 320 mμ because *trans*-$Pt(NH_3)_4Br_2^{2+}$ has a considerably larger molar absorptivity than *trans*-$Pt(NH_3)_4ClBr^{2+}$ at this wave length; this leads to large uncertainties in the values obtained.

Results

A general rate law for the forward and reverse steps of reactions 4 and 5 is presented in eq. 6. The $[Pt(NH_3)_4^{2+}]$-independent term was observed only in

$$d[Pt(NH_3)_4XY^{2+}]/dt = (k[Pt(NH_3)_4^{2+}] + k')[Pt(NH_3)_4XZ^{2+}][Y^-] \tag{6}$$

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(3) J. V. Rund, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 658 (1964).

(4) "Gmelin's Handbuch der Anorganischen Chemie," 68D Verlag Chemie, Weinheim/Bergstrasse, 1957, pp. 491, 501.

(5) R. N. Keller, *Inorg. Syn.*, **2**, 251 (1963).

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

(7) A. J. Poë, *J. Chem. Soc.*, 183 (1963).

TABLE I

RATE DATA

trans-Pt(NH$_3$)$_4$Cl$_2$$^{2+}$ + Br$^-$ → *trans*-Pt(NH$_3$)$_4$ClBr^{2+} + Cl$^-$

[Pt-(NH$_3$)$_4$$^{2+}$],^{a} M × 10^5	k_{obsd}, sec.$^{-1}$ × 10^4	k, M^{-2} sec.$^{-1}$ × 10^{-2}	[Pt-(NH$_3$)$_4$$^{2+}$],^{a} M × 10^5	k_{obsd}, sec.$^{-1}$ × 10^4	k, M^{-2} sec.$^{-1}$ × 10^{-2}
	25.0°^{b}			35.0°^{b}	
4.75	2.04^c	1.08	4.75	7.9	1.66
4.75	4.4	1.15	9.50	15.8	1.66
4.75	7.7^d	1.02		45.0°^{b}	
4.75	10.1^e	1.06	4.75	12.4	2.60
9.50	8.3	1.10	9.50	24.3	2.56
14.3	11.5	1.01			
19.0	17.8	1.17			

^{a} [Pt(IV)] = 1.30 × 10^{-3} M, [H$^+$] = 5.0 × 10^{-3} M, μ = 0.20 M. ^{b} [Br$^-$] = 0.080 M. ^{c} [Br$^-$] = 0.0400 M. ^{d} [Br$^-$] = 0.160 M. ^{e} [Br$^-$] = 0.200 M.

TABLE II

RATE DATA

trans-Pt(NH$_3$)$_4$ClBr^{2+} + Br$^-$ → *trans*-Pt(NH$_3$)$_4$Br$_2$$^{2+}$ + Cl$^-$

[Pt-(NH$_3$)$_4$$^{2+}$],^{a} M × 10^6	k_{obsd}, sec.$^{-1}$ × 10^4	k, M^{-2} sec.$^{-1}$ × 10^{-4}	[Pt-(NH$_3$)$_4$$^{2+}$],^{a} M × 10^6	k_{obsd}, sec.$^{-1}$ × 10^4	k, M^{-2} sec.$^{-1}$ × 10^{-4}
	25.0°^{b,c}		10.0	5.3^i	2.36
2.50	22.2	1.83	15.0	15.0	2.31
3.75	33.^{d}	1.93	20.0	19.2	2.26
5.00	41.	1.86	20.0	10.0^i	2.35
10.0	7.6^e	1.91	30.0	14.3^i	2.29
10.0	11.4^f	1.90		45.0°^{i,j}	
10.0	15.1^g	1.86	10.0	6.5	2.62
15.0	11.2^e	1.87	15.0	9.3	2.67
20.0	15.4^e	1.92	20.0	12.3	2.77
	35.0°^{e,h}		25.0	14.7	2.68
5.0	5.3	2.10	30.0	17.3	2.67
10.0	10.5	2.34			

^{a} [Pt(IV)] = 5.0 × 10^{-5} M, [H$^+$] = 5.0 × 10^{-3} M, μ = 0.20 M. ^{b} k' = 1.0 × 10^{-2} M^{-1} sec.$^{-1}$. ^{c} [Br$^-$] = 4.00 × 10^{-2} M. ^{d} [Br$^-$] = 2.00 × 10^{-2} M. ^{e} [Br$^-$] = 4.00 × 10^{-3} M. ^{f} [Br$^-$] = 6.00 × 10^{-3} M. ^{g} [Br$^-$] = 8.0 × 10^{-3} M. ^{h} k' = 3 × 10^{-2} M^{-1} sec.$^{-1}$. ^{i} [Br$^-$] = 2.00 × 10^{-3} M. ^{j} k' = 6 × 10^{-2} M^{-1} sec.$^{-1}$.

TABLE III

RATE DATA

trans-Pt(NH$_3$)$_4$ClBr^{2+} + Cl$^-$ → *trans*-Pt(NH$_3$)$_4$Cl$_2$$^{2+}$ + Br$^-$

[Pt-(NH$_3$)$_4$$^{2+}$],^{a} M × 10^4	k_{obsd}, sec.$^{-1}$ × 10^4	k, M^{-2} sec.$^{-1}$	[Pt-(NH$_3$)$_4$$^{2+}$],^{a} 10^4	k_{obsd}, sec.$^{-1}$ × 10^4	k, M^{-2} sec.$^{-1}$
	25.0°^{b}		17.5	19.5	11.2
10.0	6.4	6.4	20.0	22.8	11.4
15.0	9.4	6.3	22.5	27.0	12.0
20.0	12.6	6.3			
25.0	15.9	6.3		45.0°^{b}	
30.0	18.7	6.2	3.75	10.3^c	19.5
			5.00	9.5	19.0
	35.0°^{b}		6.25	14.5^d	19.3
10.0	11.5	11.5	7.50	15.6	20.8
15.0	17.8	11.9	8.75	17.9	20.4
			10.00	17.4^e	21.7

^{a} [Pt(IV)] = 7.0 × 10^{-4} M, [H$^+$] = 5.0 × 10^{-3} M, μ = 0.20 M. ^{b} [Cl$^-$] = 0.100 M. ^{c} [Cl$^-$] = 0.140 M. ^{d} [Cl$^-$] = 0.120 M. ^{e} [Cl$^-$] = 0.080 M.

TABLE IV

RATE DATA

trans-Pt(NH$_3$)$_4$Br$_2$$^{2+}$ + Cl$^-$ → *trans*-Pt(NH$_3$)$_4$ClBr^{2+} + Br$^-$

[Pt-(NH$_3$)$_4$$^{2+}$],^{a} M × 10^5	k_{obsd}, sec.$^{-1}$ × 10^3	k, M^{-2} sec.$^{-1}$ × 10^{-3}	[Pt-(NH$_3$)$_4$$^{2+}$],^{a} M × 10^5	k_{obsd}, sec.$^{-1}$ × 10^3	k, M^{-2} sec.$^{-1}$ × 10^{-3}
	25.0°^{b}			45.0°^{d}	
5.0	1.23^c	4.2	5.0	9.5	9.1
10.0	1.45	4.3	7.5	13.7	8.7
15.0	2.11	4.2	10.0	18.0	8.6
20.0	2.77	4.1	12.5	21.5	8.2
	35.0°^{b}				
5.0	1.02	6.1			
7.5	1.54	6.2			
10.0	2.09	6.3			
15.0	3.1	6.1			

^{a} [Pt(IV)] = 5.0 × 10^{-5} M, [H$^+$] = 5.0 × 10^{-3} M, μ = 0.20 M. ^{b} [Cl$^-$] = 3.34 × 10^{-3} M. ^{c} [Cl$^-$] = 5.84 × 10^{-3} M. ^{d} [Cl$^-$] = 2.09 × 10^{-3} M.

TABLE V

RATE CONSTANTS AT 25.0° AND ACTIVATION PARAMETERS

Complex reactant	Entering halide	ΔH*, kcal./mole	ΔS*, e.u./mole	k, M^{-2} sec.$^{-1}$
Pt(NH$_3$)$_4$Cl$_2$$^{2+}$	Br$^-$	8	−24	108
Pt(NH$_3$)$_4$ClBr^{2+}	Br$^-$	3	−30	1.9 × 10^4
Pt(NH$_3$)$_4$ClBr^{2+}	Cl$^-$	11	−20	6.3
Pt(NH$_3$)$_4$Br$_2$$^{2+}$	Cl$^-$	6	−22	4.2 × 10^3

the reaction of *trans*-Pt(NH$_3$)$_4$ClBr^{2+} with Br$^-$. In these reactions the concentration of Pt(NH$_3$)$_4$$^{2+}$ was maintained at a sufficiently high level such that the Pt(II)-independent process contributed little to the observed rate. Therefore, k' values are rather inaccurate and additional studies are necessary to ascertain whether a simple second-order rate law adequately describes the Pt(II)-independent path.

Rate data for the reactions are presented in Tables I–IV. A summary of third-order rate constants at 25.0° and activation parameters is found in Table V. Many of the kinetic experiments presented in Tables I–IV have been repeated and replicates agreed within a few per cent. Several preparations of platinum(IV) and platinum(II) complexes were used during the studies; agreement in the resulting kinetic runs was good; discrepancies in rate data from different preparations of platinum(IV) complexes, when observed, could be traced to [Pt(NH$_3$)$_4$$^{2+}$] present as an impurity. There was no evidence to suggest light catalysis.

Reaction 7 has been reported to be complete in 5

$$trans\text{-Pt(NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{Br}_2{}^{2+} + \text{Cl} \longrightarrow trans\text{-Pt(NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{BrCl}^{2+} + \text{Br}^- \quad (7)$$

min. in the presence of added Pt(NH$_2$CH$_2$CH$_2$NH$_2$)$_2$$^{2+}$.[8] The rate was reported to be first-order in platinum(IV) complex and chloride ion and catalyzed by Pt(NH$_2$CH$_2$CH$_2$NH$_2$)$_2$$^{2+}$. These data are in accord with our observations on the corresponding tetraammine complex.

Equilibrium constants for reactions 4 and 5 were calculated from the ratios of appropriate rate constants. Values for the equilibrium constants were independently determined from equilibrium studies patterned after the studies of Poë.[7] The results of these studies and calculations are reported in Table VI. Poë[7] determined the equilibrium constants for reactions analogous to (4) and (5) in which four ammonias in each complex

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[8] F. Basolo, A. F. Wilks, R. G. Pearson, and R. G. Wilkins, *J. Inorg. Nucl. Chem.*, **6**, 161 (1958).

TABLE VI

EQUILIBRIUM CONSTANTS FOR REACTIONS 4 AND 5 AT 25.0°

	k_f/k_r	Equil. expts.	Av.
K_1	17	16	16
K_2	4.5	4.3	4.4

were replaced with two ethylenediamines. Values of K_1 and K_2 reported were 11.5 and 4.0. Grinberg and co-workers have reported standard oxidation–reduction potentials for half-cells 8 and 9.[9] A value of K_1K_2 for

$$trans\text{-Pt(NH}_3)_4\text{Cl}_2{}^{2+} + 2e \rightleftharpoons \text{Pt(NH}_3)_4{}^{2+} + 2\text{Cl}^- \quad E° = 0.600 \text{ v.} \qquad (8)$$

$$trans\text{-Pt(NH}_3)_4\text{Br}_2{}^{2+} + 2e \rightleftharpoons \text{Pt(NH}_3)_4{}^{2+} + 2\text{Br}^- \quad E° = 0.538 \text{ v.} \qquad (9)$$

reactions 4 and 5 can be calculated from these potentials. The result, 130, is in reasonable agreement with our $K_1K_2 = 70$.

TABLE VII

EXPERIMENTAL DATA AND CALCULATED RESULTS IN THE DETERMINATION OF K_1 AND K_2[a]

$$K_1 = \frac{(\epsilon - \epsilon_{\text{Cl}_2})[\text{Cl}^-]/[\text{Br}^-]}{\epsilon_{\text{ClBr}} - \epsilon + K_2(\epsilon_{\text{Br}_2} - \epsilon)[\text{Br}^-]/[\text{Cl}^-]}$$

$$K_2 = \frac{\{(\epsilon - \epsilon_{\text{Cl}_2})[\text{Cl}^-]/[\text{Br}^-]\} + K_1(\epsilon - \epsilon_{\text{ClBr}})}{K_1(\epsilon_{\text{Br}_2} - \epsilon)[\text{Br}^-]/[\text{Cl}^-]}$$

$[\text{Cl}^-]_0$[b]	$[\text{Br}^-]_0$	$[\text{Cl}^-]/[\text{Br}^-]$	ϵ_{300}[c]	ϵ_{320}	K_1	K_2 when ϵ_{ClBr} is 320	270	260	230
0.1920	0.0080	18.54	372	287	17.2	3.52	4.39	4.57	5.09
0.1900	0.0100	15.50	395	318	16.0	3.37	4.13	4.28	4.73
0.1867	0.0133	11.84	443	381	15.6	3.44	4.05	4.17	4.54
0.1800	0.0200	7.90	519	500	15.1	3.83	4.32	4.42	4.72
0.1750	0.0250	6.48	566	581	16.3	3.85	4.27	4.35	4.60
0.1714	0.0286	5.58	591	632	15.6	3.85	4.23	4.31	4.54
0.1667	0.0333	4.74	626	696	15.5	3.94	4.29	4.36	4.57
0.1600	0.0400	3.86	664	778	16.4	4.05	4.37	4.44	4.63
0.1500	0.0500	2.90	708	880	14.7	4.06	4.35	4.35	4.58
					$K_1 = 15.8$				
					$\bar{K}_2$	3.77	4.37	4.27	4.67
					$\Sigma\lvert\bar{K}_2 - K_2\rvert^2$	0.54	0.10	0.10	0.24
					K_2		4.32		

[a] $[\text{Pt(IV)}] = 6.67 \times 10^{-4}\ M$, $[\text{H}^+] = 5.0 \times 10^{-3}\ M$, $\mu = 0.20\ M$. [b] $[\text{Cl}^-]_0$ = moles of NaCl added/liter of solution. [c] ϵ = absorbance/[Pt(IV)].

The equilibrium constants K_1 and K_2 are defined in eq. 10 and 11. The molar absorptivities of *trans*-

$$K_1 = [\text{Pt(NH}_3)_4\text{ClBr}^{2+}][\text{Cl}^-]/[\text{Pt(NH}_3)_4\text{Cl}_2{}^{2+}][\text{Br}^-] \qquad (10)$$

$$K_2 = [\text{Pt(NH}_3)_4\text{Br}_2{}^{2+}][\text{Cl}^-]/[\text{Pt(NH}_3)_4\text{ClBr}^{2+}][\text{Br}^-] \qquad (11)$$

$\text{Pt(NH}_3)_4\text{Cl}_2{}^{2+}$, ϵ_{Cl_2}, were found to be 92 and 88 at 300 and 320 mμ, respectively. The molar absorptivity of *trans*-$\text{Pt(NH}_3)_4\text{ClBr}^{2+}$, ϵ_{ClBr}, at 300 mμ is 570. The apparent molar absorptivity of *trans*-$\text{Pt(NH}_3)_4\text{Br}_2{}^{2+}$, ϵ_{Br_2}, was found to obey eq. 12 and 13, when $[\text{Br}^-]$ was in the range 0.005–0.5 M, but was nonlinear at higher

$$\epsilon_{\text{Br}_2} \text{ at 300 m}\mu = 800 + 1580[\text{Br}^-] \qquad (12)$$

$$\epsilon_{\text{Br}_2} \text{ at 320 m}\mu = 980 + 1330[\text{Br}^-] \qquad (13)$$

bromide concentrations. The dependence of ϵ_{Br_2} on $[\text{Br}^-]$ is discussed in ref. 7.

Experimental data and pertinent calculated results for the determination of K_1 and K_2 are presented in Table VII. K_1 was calculated from data at 300 mμ using a trial value of K_2 of 4.49, which was found in the kinetic studies. A recalculation used $K_2 = 4.32$. K_2 was calculated from data at 320 mμ. Since a value of ϵ_{ClBr} at 320 mμ is not accurately known, calculations were made using a number of reasonable values. The value of ϵ_{ClBr} which gave the most consistent set of K_2 values was chosen. K_2 is not markedly sensitive to ϵ_{ClBr}.

Discussion

The rate data collected on the forward and reverse processes in reactions 4 and 5 are consistent with the mechanism (eq. 1–3) proposed by Basolo and co-workers for similar reactions. The rate data for reaction 5 indicate that in this one reaction a $\text{Pt(NH}_3)_4{}^{2+}$-independent process is also operative. It is very unlikely that the platinum(IV) complex could contain enough platinum(II) impurity to produce the residual rate. Moreover, the platinum(II)-independent reaction is much more temperature dependent than the normal reaction.

From the rate data in Table V it is apparent that reactions in which bromine is *trans* to the leaving group are much faster than those in which chlorine is in the *trans* position. The rate change is primarily due to a 5 kcal./mole difference in activation enthalpy and is reduced by a small opposing change in activation entropy (2–6 e.u./mole). In the mechanism outlined in eq. 1–3 the halogen opposite the leaving atom functions as a bridging atom; therefore, this term will be used in subsequent discussions.

Studies on the replacement of an ammonia molecule in halopentaammineplatinum(IV) complexes by a halide ion are also consistent with a mechanism similar to that outlined in eq. 1–3.[1] In studies on these systems an increase in ΔH^* of 5 kcal./mole was observed when the bridging atom was changed from bromine to chlorine. The activation entropy became one unit more positive during the same change. Differences in the bridging atom produce very similar changes in activation parameters of reactions of both *trans*-dihalotetraammine and halopentaammine complexes of platinum(IV).

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[9] Reference 4, p. 41.

The ΔH^* of 3 kcal./mole observed for reaction 5 is very small. Since it has been reported[10] that hydration effects markedly influence enthalpy changes in reactions of this type, it is dangerous to attribute this enthalpy change to differences in bonding between the starting material and activated complex. Yet it seems reasonable that this small value of ΔH^* indicates that the activated complex has a geometry more closely resembling the reactants, Cl–Pt–Br--Pt--Br^{3+}, than the products, Cl--Pt--Br–Pt–Br^{3+}.

The ratio of the average equilibrium constants reported in Table VI is 3.6. This is rather close to the ratio of 4 which is expected on statistical grounds. The values of K_1 and K_2 show that bromide is coordinated in preference to chloride; this is in line with previous equilibrium studies and thermodynamic data.[10,11] The data show that there is both an equilibrium and a kinetic "*trans* effect" in these systems, with bromide being the better *trans*-director. The equilibrium *trans* effect is very small, but the kinetic effect is quite large. It should be noted that the kinetic *trans* effect is best explained in terms of the bridging ability of the bromine atom; this explanation is quite different from those given to explain the *trans* effect as observed in platinum(II) systems.

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Synthesis and Aquation Kinetics of *cis*-Chloroisothiocyanatobis(ethylenediamine)chromium(III) Cation and of *cis*- and *trans*-Isothiocyanatoaquobis(ethylenediamine)chromium(III) Cations[1]

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The new complexes *cis*-Cr(en)$_2$(NCS)Cl$^+$ and *cis*- and *trans*-Cr(en)$_2$(OH$_2$)NCS^{+2} have been synthesized and their visible absorption spectra and their aquation kinetics have been investigated in acid solution in the dark. In 0.001–1.0 F HClO$_4$ (μ = 0.1–1.0, NaClO$_4$) the rate constant for aquation of *cis*-Cr(en)$_2$(NCS)Cl$^+$ is $(8.1 \pm 0.4) \times 10^{-5}$ sec.$^{-1}$ at 25°, with $E_a = 20.5 \pm 1.3$ kcal. mole^{-1} and log $PZ = 10.9 \pm 1.0$ (sec.$^{-1}$); aquation proceeds *via* Cl$^-$ release ($\leqslant 4\%$ SCN$^-$ release), the directly-formed products of Cl$^-$ release being *cis*-Cr(en)$_2$(OH$_2$)NCS^{+2} (98 ± 2%) and *trans*-Cr(en)$_2$(OH$_2$)NCS^{+2} (2 ± 2%). At 25° $k = (1.5 \pm 0.2) \times 10^{-6}$ sec.$^{-1}$ for aquation of *cis*-Cr(en)$_2$(OH$_2$)NCS^{+2} in 0.75 F HClO$_4$, the products apparently being Cr(en)(OH$_2$)$_3$NCS^{+2} and *cis*-Cr(en)$_2$(OH$_2$)$_2$$^{+3}$, the latter possibly formed partly or wholly *via* production of the *trans* isomer followed by relatively fast isomerization. An upper limit of $k \leqslant 2 \times 10^{-8}$ sec.$^{-1}$ was found for aquation of *trans*-Cr(en)$_2$(OH$_2$)NCS^{+2} in 0.8 F HClO$_4$ at 25°.

The coordination complexes *cis*-chloroisothiocyanatobis(ethylenediamine)chromium(III) and *cis*- and *trans*-isothiocyanatoaquobis(ethylenediamine)chromium(III) apparently have not been previously reported. We report here the synthesis and characterization of these new cations, their visible absorption spectra, and the results of our investigations of the aquation kinetics of these complexes in acid solution in the dark, undertaken to allow comparisons to be made with the extensively studied chloro,[2-6] bromo,[7] and fluoro[8] analogs, as well as with the Co(III) analogs to the extent that information on them is available.

Experimental

***cis*-Isothiocyanatoaquobis(ethylenediamine)chromium(III) Cation.**—This ion was prepared in solution by dissolving 0.8 g. of *cis*-[Cr(en)$_2$(NCS)$_2$]SCN·H$_2$O[9] in 500 ml. of 0.1 F HClO$_4$ and allowing the solution to aquate in the dark for *ca.* 8.5 hr. at 50°. The solution was cooled and passed through a 10-cm. × 1-cm. diameter column of H$^+$ Dowex AG50W-X8 (100–200 mesh) cation-exchange resin to adsorb all Cr cationic species, then 900

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