TABLE I
X-RAY POWDER DIFFRACTION DATA
(d VALUES IN Å)

$(CH_3)_3PtI$			
Yellow form	White form	$[(CH_3)_3Pt]_2SO_4$	$(CH_3)_3PtNO_3$
		11.30 s	5.91 m
		10.40 s	5.72 s
8.59 m	8.60 w	6.41 vw	5.26 s
8.13 s	8.15 s	6.17 m	4.64 s
7.74 m	7.75 m	5.55 vs	4.03 m
7.24 m	7.26 m	5.27 vs	3.81 w
6.32 s	6.30 s	5.05 s	3.61 w
5.06 w	5.07 w	4.91 s	3.30 w
4.61 w	4.64 w	4.45 m	3.23 w
4.36 w	4.34 w	4.18 w	3.17 w
...	4.04 vw	3.38 vw	2.95 vw
3.79 vw	3.79 vw	3.58 vw	2.90 vw
3.67 vw	...	3.42 vw	2.85 w
3.43 vw	3.47 vw	3.38 m	2.78 vw
3.33 vw	3.34 vw	3.26 m	2.74 w
3.22 w	3.23 s	3.05 s, b	2.70 vw
3.14 s	3.15 m	2.84 vw	2.51 vw
3.03 m	3.05 m	2.73 m	2.47 vw
2.98 m	...	2.68 s	2.44 s
2.91 m	2.91 s	2.53 vw	2.34 m
2.83 m	2.82 s	2.47 m	2.30 w
2.69 vw	...	2.43 m	2.20 w
2.62 w	2.62 w	2.40 vw	2.15 w
2.57 vw	2.57 vw	2.35 w	2.07 vvw
2.54 vw	...	2.29 w	2.02 m
2.49 vw	2.49 s	2.20 w	1.98 w
2.41 s	2.41 m	2.15 s	1.93 w
2.38 vw	...	2.08 vw	1.86 m
2.36 vw	2.36 m	2.03 w	1.83 m
2.30 w	2.30 vw	1.99 w	1.81 m
2.22 w	2.22 w	1.96 m	1.65 m
2.20 w	2.19 m	1.90 vw	1.59 vw
2.16 w	...	1.87 w	1.56 m
2.11 w	2.10 w	1.80 w	1.52 vw
2.05 m	2.06 w	1.73 m	1.47 vvw
2.03 vw	2.03 vw	1.66 vw	1.45 vw
1.98 m	1.97 m	1.62 w	1.43 vw
1.89 vw	1.90 w	1.60 w	1.37 s
1.88 vw	...	1.58 w	1.35 m
1.87 vw	1.86 w	1.56 w	1.28 w
1.84 vw	...	1.54 w	1.24 m
1.78 vw	1.76 vw	1.50 w	1.14 w
...	1.73 vw	1.48 vw	1.04 w
...	1.71 vw	1.43 w, b	
...	1.65 vw	1.40 vw	
1.62 vw	1.62 vw	1.38 cw	
1.60 vw	1.60 vw	1.35 w	
	1.58 vw	1.34 w	
	1.55 vw	1.30 w, b	
		1.25 vw	

It appears that the white and yellow forms are identical, except for some minor impurity, possibly iodine. It was not possible to isolate the impurity, although, when yellow $(CH_3)_3PtI$ is converted to the sulfate or is dissolved in benzene, a small dark residue remains. We were unable to collect enough of the residue to analyze. The yellow compound can be whitened considerably if a benzene solution is treated with a silver salt and the trimethylplatinum(IV) iodide is recovered.

Clegg and Hall,[12] Glass and Tobias,[13] and Kite, *et al.*,[6] have concluded that the trimethylplatinum(IV) ion is unassociated and octahedral in water and our conductance data agree to the extent that $(CH_3)_3PtNO_3$ is a strong 1–1 electrolyte and $[(CH_3)_3Pt]_2SO_4$ is a typical 1–2 sulfate. The Λ_0 values were determined by extrapolation by the method of Owen,[14] and the method of least squares was employed in fitting the data. The conductance results are given below.

$N \times 10^3$ and Λ (ohm^{-1} cm^2 equiv^{-1}) for $(CH_3)_3PtNO_3$: 38.32, 95.4; 33.53, 96.7; 25.67, 98.8; 22.46, 99.8; 19.65, 100.7; 14.74, 102.6; 11.05, 104.2; 7.254, 106.0; 6.346, 106.6; 5.553, 107.0; 4.858, 107.6; 4.251, 108.0; 3.188, 108.9; 2.390, 109.6; 0.840, 111.4; 0.525, 112.1; $\Lambda_0 = 114.3 \pm 0.06$.

$N \times 10^3$ and Λ (ohm^{-1} cm^2 equiv^{-1}) for $[(CH_3)_3Pt]_2SO_4$: 24.44, 86.8; 22.22, 88.1; 18.14, 90.4; 15.68, 92.0; 10.87, 95.6; 8.804, 97.5; 7.120, 99.0; 6.346, 99.9; 5.334, 101.1; 4.870, 101.6; 3.528, 103.5; 3.004, 104.5; 2.478, 105.5; 1.981, 106.6; 1.610, 107.4; 1.051, 109.0; $\Lambda_0 = 117.5 \pm 0.09$.

Infrared spectra of the nitrate and sulfate agree with those previously reported[15,16] when they are measured in mulls, but in KBr disks only the spectrum of $(CH_3)_3PtBr$ is observed.

---

[12] D. E. Clegg and J. R. Hall, *Spectrochim. Acta*, **21**, 357 (1965).

[13] G. E. Glass and R. S. Tobias, *J. Am. Chem. Soc.*, **89**, 6371 (1967).

[14] B. B. Owen, *ibid.*, **61**, 1393 (1939).

[15] M. N. Hoechstetter, *J. Mol. Spectry*, **13**, 407 (1964).

[16] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
EMORY UNIVERSITY, ATLANTA, GEORGIA 30322

The Interconversion of the *trans*-Dichlorotetraammineplatinum(IV) and *trans*-Chloropyridinetetraammineplatinum(IV) Cations

BY RONALD C. JOHNSON AND EUGENE R. BERGER

Received January 25, 1968

A variety of substitution reactions of *trans*-$Pt(NH_3)_4Cl_2^{2+}$ and similar complexes are catalyzed by $Pt(NH_3)_4^{2+}$ and have been postulated to proceed *via* an inner-sphere redox mechanism.[1] Zvyagintsev and Shubochkina however have reported that the rates of reactions of a number of such complexes with ammonia and pyridine are unaffected by the addition of $Pt(NH_3)_4^{2+}$.[2] One reaction (1) on which they reported

$$trans\text{-}Pt(NH_3)_4Cl_2^{2+} + NH_3 \longrightarrow Pt(NH_3)_5Cl^{3+} + Cl^- \quad (1)$$

has been restudied.[3] The results indicated that reaction 1 is catalyzed by $Pt(NH_3)_4^{2+}$ and does not proceed cleanly in the basic solutions used in ref 2.

The present study was initiated in order to determine whether the results reported in ref 2 for reaction 2

$$trans\text{-}Pt(NH_3)_4Cl_2^{2+} + py \longrightarrow trans\text{-}Pt(NH_3)_4pyCl^{3+} + Cl^- \quad (2)$$

are valid (py = pyridine). In the earlier study of this reaction, the products were not characterized and the pH was not controlled.

Experimental Section

The preparation and analyses of *trans*-$[Pt(NH_3)_4Cl_2](NO_3)_2$ and $[Pt(NH_3)_4](ClO_4)_2$ have been described in an earlier paper.[3]

Preparation of *trans*-$[Pt(NH_3)_4pyCl](NO_3)_3$.—One gram (2.16

---

[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, pp 494–497.

[2] O. E. Zvyagintsev and E. F. Shubochkina, *Zh. Neorgan. Khim.*, **6**, 2029 (1961).

[3] R. R. Rettew and R. C. Johnson, *Inorg. Chem.*, **4**, 1565 (1965).

mmol) of *trans*-[$Pt(NH_3)_4Cl_2](NO_3)_2$ and 0.02 g (0.04 mmol) of [$Pt(NH_3)_4](ClO_4)_2$ were dissolved in 25 ml of H_2O. To this solution was added first 0.1 ml (1 mmol) of concentrated HNO_3 and then 1.0 g (13 mmol) of pyridine. Twenty-five milliliters of an $AgNO_3$ solution (0.367 g; 2.16 mmol of $AgNO_3$) was added in small portions over a period of 3 days. The reaction mixture was kept in the dark at room temperature. The AgCl formed was collected by filtration and the solution was freeze-dried. The product was carefully washed with acetone, dried, and redissolved in 15 ml of H_2O. An insoluble residue was removed. The white product (0.90 g, 73% yield) was collected by evaporation of the H_2O at room temperature using vacuum. *Anal.* Calcd for [$Pt(NH_3)_4(C_5H_5N)Cl](NO_3)_3$: Pt, 34.6; Cl, 6.27; py, 14.0; C, 10.6; H, 3.02. Found: Pt, 34.7; Cl, 6.71; py, 13.0; C, 9.90; H, 3.75. Platinum was determined by ignition in the presence of NH_4Cl. Chloride was determined by Volhard titration after a zinc–acetic acid reduction step. Pyridine was analyzed spectrophotometrically at 255.5 mμ as pyH^+ after reaction of the complex with HCl. The spectra of dilute solutions of *trans*-[$Pt(NH_3)_4pyCl](NO_3)_3$ did not change on standing for several weeks.

Preparation of *trans*-[$Pt(NH_3)_4Cl(C_2H_3O_2)](NO_3)_2$.—Five milliliters of a solution containing 0.32 g (0.56 mmol) of *trans*-[$Pt(NH_3)_4pyCl](NO_3)_3$ was mixed with 30 ml of glacial acetic acid. A white crystalline product began to form after a few hours. The solution was evaporated to half its volume in a desiccator over NaOH. The product (0.25 g, 90% yield) was collected by filtration. *Anal.* Calcd for [$Pt(NH_3)_4Cl(C_2H_3O_2)](NO_3)_2$: Pt, 40.5; Cl, 7.38; C, 4.98; H, 3.12. Found: Pt, 40.5; Cl, 7.32; C, 5.15; H, 3.18. The spectrum of the product has a shoulder centered at about 295 mμ and an intense maximum at 205 mμ.

Kinetic Measurements.—Kinetic data were taken on a Cary 14 or on a Beckmann DU spectrophotometer modified with a Gilford absorbance indicator. The cell compartments were thermostated to ±0.02°. Rate data on reaction 2 were obtained at 310 mμ. The pH of some reaction mixtures was controlled with tris(hydroxymethyl)aminomethane–perchloric acid buffers. The spectrum of *trans*-$Pt(NH_3)_4Cl_2^{2+}$ in these buffers does not change in 1.5 hr in the absence of pyridine. The reverse of reaction 2 in acid solutions was studied at 255.5 mμ, where pyH^+ absorbs strongly. In neutral solutions studies were made at 265 mμ, a wavelength at which reactants absorb appreciably more than products. The ratio of concentrations of entering ligand to Pt(IV) was sufficiently large that pseudo-first-order kinetic behavior was expected. In acidic solutions $HClO_4$ was used to control ionic strength and acidity. In neutral solutions $NaNO_3$ was used to control ionic strength. No precautions were taken to avoid exposure of reaction mixtures to light. That the product of the reverse of reaction 2 was *trans*-$Pt(NH_3)_4Cl_2^{2+}$ was confirmed by isolation of the sparingly soluble chloride salt from some reaction mixtures. The infinite time spectra were also consistent with the expected products; however, py or pyH^+ bands obscure the most characteristic part of the spectrum of *trans*-$Pt(NH_3)_4Cl_2^{2+}$.

Absorbance *vs.* time data were analyzed at the Emory Biomedical Data Processing Center using a Gauss–Newton fit to the equation: $A = A_\infty + (A_0 - A_\infty)\exp(-kt)$. Twenty data points regularly spaced over at least 4 half-lives were used for each kinetic run. The standard deviation in individual k's was less than 2% of k in almost all runs and less than 1% in most. Data for reaction 2 at low pyridine concentrations exhibited slightly larger deviations, and it is probable that these runs do not follow a simple first-order rate law. Kinetic runs could be reproduced to within ±10% and normally agreed to within a few per cent.

Equilibrium Measurements.—Solutions having these compositions were prepared: [*trans*-$Pt(NH_3)_4pyCl^{3+}$]: (1) 1.02×10^{-2} *M*, (2) 1.06×10^{-2} *M*; [*trans*-$Pt(NH_3)_4Cl_2^{2+}$]: (1) 7.7×10^{-4} *M*, (2) 8.0×10^{-4} *M*; [NaCl]: (1) 9.68×10^{-3} *M*, (2) 10.0×10^{-3} *M*; [$Pt(NH_3)_4^{2+}$]: (1) 1.05×10^{-3} *M*, (2) 1.17×10^{-3} *M*. A little NaOH solution was added to neutralize both reaction mixtures. The pH values of the solutions (after NaOH had been added) were 5 and 7. After the reaction, both solutions had a pH of 7. The solutions were kept in the dark at 25.0° until the spectrum of a sample of the solution showed no further changes in absorbance at 335 mμ (3 days). Ionic chloride in the solutions was then determined using a modified Volhard titration: (1) 2.47×10^{-3} *M*, (2) 2.32×10^{-3} *M*. A titration for chloride on the following day gave a similar result. Titrations performed at the start of the experiment were consistent with the amount of NaCl added. Equilibrium constants for reaction 2 calculated from these data are 0.13 and 0.10. Since the value of the constant is sensitive to relatively small errors in the concentrations of platinum complexes and may also be somewhat pH dependent, a realistic value of the constant at 25.0° in neutral solution is 0.12 ± 0.03. The catalyst [$Pt(NH_3)_4](ClO_4)_2$ was not added initially to solution 1. However, when the absorbance of this solution was unchanged after 2 days, solid catalyst was added. The absorbance change in both experiments was greater than 0.4 absorbance unit at 335 mμ.

The small value of K found for reaction 2 is consistent with another qualitative experiment. A reaction mixture containing 0.011 *M* *trans*-[$Pt(NH_3)_4Cl_2](NO_3)_2$ and 0.068 *M* pyridine was allowed to react in the dark at room temperature for 11 days. (On the basis of both our work and that of ref 2 this is over 20 half-lives.) The solution was freeze-dried. The product was washed carefully with acetone and dried under vacuum. The spectrum of an aqueous solution exhibited clearly the 335-mμ maximum of *trans*-$Pt(NH_3)_4Cl_2^{2+}$. The absorbance in the 250–260-mμ region indicated that pyridine in some form was also present. As a control experiment a solution of *trans*-[$Pt(NH_3)_4pyCl](NO_3)_3$ (0.011 *M*) and NaCl (0.020 *M*) was prepared and freeze-dried. The product was carefully washed with acetone and dried under vacuum. The spectrum of a solution of this product did not have a maximum in the 335-mμ region and did have the characteristic spectrum of *trans*-$Pt(NH_3)_4pyCl^{3+}$ in the 250–260-mμ region.

Results

The new compound *trans*-[$Pt(NH_3)_4pyCl](NO_3)_3$ was synthesized and characterized. Its ultraviolet spectrum and that of py and pyH^+ are shown in Figure 1.

Rate data for the reverse of reaction 2 are presented in Table I. At a fixed pH the data are consistent with the third order rate law

$$-d[Pt(NH_3)_4pyCl^{3+}]/dt = k_3[Pt(NH_3)_4pyCl^{3+}][Pt(NH_3)_4^{2+}][Cl^-] \quad (3)$$

In experiments in which $Pt(NH_3)_4^{2+}$ was not added, a very slow rate was observed. A 1% $Pt(NH_3)_4^{2+}$ impurity in our *trans*-[$Pt(NH_3)_4pyCl](NO_3)_3$ would produce a rate greater than this. A slight decrease in rate was noted in neutral and slightly basic solutions. The diminished rate observed at pH 8.5 is probably due to the presence of *trans*-$Pt(NH_3)_3NH_2pyCl^{2+}$, the conjugate base of the reactant complex.

Rate data on reaction 2 are reported in Table II. Catalysis by $Pt(NH_3)_4^{2+}$ was established, and the rate constant increased as the pyridine concentration was raised, but the dependence was less than first order. Considerable additional data were collected to confirm this point. Satisfactory first-order kinetic behavior was observed except at the lowest pyridine concentration (0.1 *M*), at which, with a platinum(IV) concentration of 3.1×10^{-3} *M*, only 85% of the $Pt(NH_3)_4Cl_2^{2+}$ was converted into $Pt(NH_3)_4pyCl^{3+}$. This would account for a significant deviation from first-order kinetics.

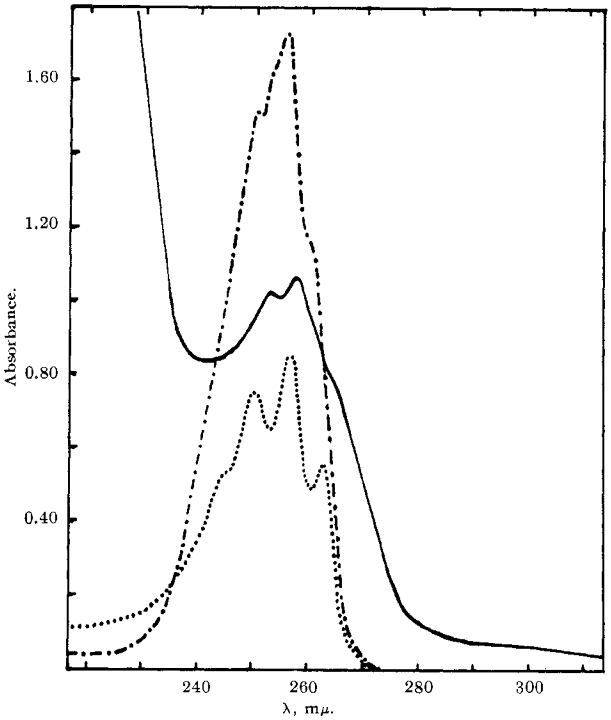

Figure 1.—The ultraviolet spectra of 3.4×10^{-4} *M* solutions of *trans*-$[Pt(NH_3)_4pyCl](NO_3)_3$ (——), pyridine (······), and pyridine in 0.067 *M* $HClO_4$ (–·–·–).

TABLE I

RATE DATA AT 25.0°

trans-$Pt(NH_3)_4pyCl^{3+} + Cl^- \longrightarrow$ *trans*-$Pt(NH_3)_4Cl_2^{2+} + py$

$10^4[Pt(NH_3)_4^{2+}]$, *M*	10^4k_{obsd}, sec^{-1}	k_3, M^{-2} sec^{-1}	$10^4[Pt(NH_3)_4^{2+}]$, *M*	10^4k_{obsd}, sec^{-1}	k_3, M^{-2}, sec^{-1}
2.03[a]	3.5[b]	8.7	...[h]	0.14[b]	...
4.05[a]	6.7[b]	8.3	2.44[h]	3.1[b]	6.4
8.1[a]	13.3[b]	8.2	4.9[h]	6.2[b]	6.3
8.1[a]	6.6[c]	8.2	4.9[h]	2.9[c]	5.9
8.1[a]	3.2[d]	7.9	9.8[h]	6.1[c]	6.2
8.1[e]	2.3[f]	5.7	9.8[h]	3.2[d]	6.5
8.1[e]	13.0[g]	8.0	5.1[i]	3.0[b]	2.9
			10.2[i]	5.5[b]	2.7

[a] [Pt(IV)] = 7.1×10^{-4} *M*; $[H^+] = 0.20$ *M*; $\mu = 0.20$. [b] $[Cl^-] = 0.200$ *M*. [c] $[Cl^-] = 0.100$ *M*. [d] $[Cl^-] = 0.050$ *M*. [e] [Pt(IV)] = 7.1×10^{-4} *M*; $[H^+] = 0.050$ *M*. [f] $[Cl^-] = 0.050$ *M*; $\mu = 0.05$. [g] $[Cl^-] = 0.050$ *M*; $\mu = 0.20$. [h] [Pt(IV)] = 14.6×10^{-4} *M*; $\mu = 0.20$; pH 6.0. [i] [Pt(IV)] = 14.2×10^{-4} *M*; $\mu = 0.20$; pH 8.5.

TABLE II

RATE DATA AT 22.5°

trans-$Pt(NH_3)_4Cl_2^{2+} + py \longrightarrow$ *trans*-$Pt(NH_3)_4pyCl^{3+} + Cl^-$

$10^3[Pt(NH_3)_4^{2+}]$, *M*	[py], *M*	10^5k_{obsd}, sec^{-1}	$10^3[Pt(NH_3)_4^{2+}$, *M*	[py], *M*	10^5k_{obsd}, sec^{-1}
...[a]	0.40	1.6	...[c]	0.050	0.93
6.5[a]	0.40	65	...[c]	0.10	1.15
6.5[b]	0.10	27	...[c]	0.40	1.9
3.2[b]	0.20	19	6.5[c]	0.10	20
6.5[b]	0.20	39	6.5[c]	0.10	67[d]
9.7[b]	0.20	62	6.5[c]	0.20	83[d]

[a] [Pt(IV)] = 2.4×10^{-3} *M*; $\mu = 0.19$. [b] [Pt(IV)] = 3.1×10^{-3} *M*; pH 9.0; $\mu = 0.23$. [c] [Pt(IV)] = 3.1×10^{-3} *M*; pH 9.6; $\mu = 0.21$. [d] Temperature 42°.

Discussion

The equilibrium constants for reactions 1 and 2 at 25° are, respectively, 7×10^2[4] and 0.12. The relative order of stability

$Pt(NH_3)_5Cl^{3+} \gg$ *trans*-$Pt(NH_3)_4Cl_2^{2+} >$ *trans*-$Pt(NH_3)_4pyCl^{3+}$

is therefore established.

Tetraammineplatinum(II) cation is an effective catalyst for reaction 2. The small reaction rate in its absence may be due to the presence of $Pt(NH_3)_4^{2+}$ as an impurity. Using data from Table I a maximum value for $k_2(25°)$ of 7×10^{-5} M^{-1} sec^{-1} can be calculated for the reverse of reaction 2. Using the equilibrium constant, a maximum value of 8×10^{-6} M^{-1} sec^{-1} can be assigned to reaction 2. The value cited in ref 2 is 3.0×10^{-4} M^{-1} sec^{-1}.

The fact that the rate of reaction 2 was not first order in pyridine concentration was surprising. This result could mean that pyridine and $Pt(NH_3)_4^{2+}$ form a relatively stable adduct and that an appreciable fraction of $Pt(NH_3)_4^{2+}$ exists as the adduct at [py] = 0.10 *M*. A third-order rate constant for reaction 2 at 25°, 0.76 M^{-2} sec^{-1} at pH 6.0, can be calculated from the constant for the reverse reaction and the equilibrium constant. A value of 0.42 M^{-2} sec^{-1} (22.5°) can be calculated using k_{obsd} for reaction 2 at pH 9.0, $[Pt(NH_3)_4^{2+}] = 6.5 \times 10^{-3}$ *M*, and [py] = 0.1 *M*. The latter value would be expected to be low since first-order pyridine dependence apparently will only be observed at lower pyridine concentrations.

The rates of reactions 1 and 2 in the forward direction are quite similar. At 22.5°, pH 9.6, and $\mu = 0.20$, the third-order constant for reaction 1 is 0.7.[4] A reasonable estimate for reaction 2 is 0.5 M^{-2} sec^{-1}. Third-order rate constants for the reverse reactions at 25.0°, $\mu = 0.3$, and in acidic solution, are 1.5×10^{-3}[5] and 10 M^{-2} sec^{-1}. (The latter value was obtained by extrapolation of data at $\mu = 0.05$ and 0.2.) The relative instability of *trans*-$Pt(NH_3)_4pyCl^{3+}$ is reflected in the rapid rate at which pyridine is displaced.

Since pyridine is a base and is fairly easily displaced from *trans*-$Pt(NH_3)_4pyCl^{3+}$, it seemed likely that new *trans*-chloroacidotetraammine complexes could be produced from it. Groups which do not displace chloride may displace pyridine, especially in acidic solution. For example, it has been reported that the reaction of acetic acid and *trans*-$Pt(en)_2Cl_2^{2+}$ (en = ethylenediamine) yields starting materials.[6] Reaction of *trans*-$[Pt(NH_3)_4pyCl](NO_3)_3$ with acetic acid did occur and pyridine was replaced by acetate ion.

The results of this study differ considerably from those in ref 2. Since pyridine reacts only incompletely under their reaction conditions, analysis of their rate data is incorrect. The magnitude of the constants they do report suggests that $Pt(NH_3)_4^{2+}$ was present in their reaction mixtures. Their assertion that $Pt(NH_3)_4^{2+}$ does not catalyze these reactions is incorrect. It seems likely that their related studies

---

(4) R. C. Johnson and E. R. Berger, *Inorg. Chem.*, **4**, 1262 (1965).

(5) W. R. Mason and R. C. Johnson, *ibid.*, **4**, 1258 (1965).

(6) R. C. Johnson and F. Basolo, *J. Inorg. Nucl. Chem.*, **13**, 36 (1960).

which use pyridine as an entering ligand are in error for similar reasons.[7]

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

[7] O. E. Zvyagintsev and E. F. Shubochkina, *Zh. Neorgan. Khim.*, **3**, 1149 (1958); **8**, 590 (1963); **9**, 1785 (1964); O. E. Zvyagintsev, E. F. Shubochkina, and B. I. Peschevitskii, *ibid.*, **10**, 1033 (1965); B. I. Peshchevitskii and V. P. Kazakov, *ibid.*, **8**, 250 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STATE UNIVERSITY OF NEW YORK,
STONY BROOK, NEW YORK 11790

The Effect of Added Chloride Ion on the Chloropentaamminecobalt(III)–Chromium(II) Reaction[1a]

BY DAVID E. PENNINGTON AND ALBERT HAIM[1b]

Received January 25, 1968

The effect of added chloride ion on the rates of electron-transfer reactions between substitution-inert oxidants and substitution-labile reductants has been studied in several systems. It has been noted[2,3] that the rate acceleration is substantial for the outer-sphere reaction between hexaamminecobalt(III) and chromium(II),[4] whereas modest effects are observed for the inner-sphere reductions of aquo-,[2] acetato-,[5] and fumaratopentaamminecobalt(III)[5] by chromium(II). The chromium(II)-catalyzed exchange of chloride between $CrCl^{2+}$ and free chloride ions[6] and the chromium(II)-catalyzed substitution of iodide ion in CrI^{2+} by chloride ion[3] can also be viewed as examples of chloride ion effects on inner-sphere redox reactions.[3,6] A reasonable interpretation of these effects features the formation of disubstituted chromium(III) complexes according to eq 1.[3,6] For the system ML_5X^{2+}–

$$ML_5X^{2+} + Cr^{2+} + Cl^- \longrightarrow M^{2+} + 5L + CrXCl^+ \quad (1)$$

$Cr(OH_2)_5I^{2+}$, we were unable to detect the postulated intermediate $CrICl^+$,[3] presumably because its rate of disappearance by the reverse of reaction 1 and reaction 2 is too rapid compared to its rate of formation by the

$$CrXCl^+ + Cr^{2+} \longrightarrow CrCl^{2+} + Cr^{2+} + X^- \quad (2)$$

forward reaction in eq 1.

Clearly, in order to improve the possibilities of detection of the postulated intermediates $CrXCl^+$, it is necessary to increase their rates of formation and to avoid the presence of an excess of chromium(II), a known[7-10] catalyst for the partial aquation of disubstituted chromium(III) complexes. This approach appears to be feasible since a chromium(III) complex of charge +1 tentatively identified as $Cr(OOCCH{=}CHCOOH)Cl^+$ has been reported[5] as one of the products of the fumaratopentaamminecobalt(III)–chromium(II) reaction in the presence of chloride ions.

In the present note, we report a study of the effect of added chloride ion on the classic[11] inner-sphere reaction between $Co(NH_3)_5Cl^{2+}$ and Cr^{2+}. This reaction is extremely rapid ($k \sim 10^6 M^{-1}$ sec^{-1})[12] and has an added advantage in that the geometric configuration of the predicted reaction product $CrCl_2^+$ can be determined from spectrophotometric measurements.[13,14]

Experimental Section

Materials.—Chromium(II) perchlorate solutions were prepared and standardized as described previously.[3] Chloropentaamminecobalt(III) perchlorate was prepared by treating the corresponding chloride salt with perchloric acid. All other chemicals were reagent grade. Triply distilled water was used to prepare all of the solutions. All manipulations involving chromium(II) solutions were performed under an atmosphere of prepurified argon.

Stoichiometric Measurements.—Solutions containing the desired concentrations of chromium(II) and chloride ions were mixed with solutions containing an *excess* of $Co(NH_3)_5Cl^{2+}$ in a rapid-flow apparatus similar to that described by Dulz and Sutin.[15,16] The reacted solutions were collected at the waste exit of the apparatus and then added to a chilled Dowex 50-X8 (50–100 mesh, H^+ form) ion-exchange column. At the electrolyte concentrations used, the ions $Co(NH_3)_5Cl^{2+}$, $CrCl^{2+}$, and Co^{2+} were absorbed on the column, whereas $CrCl_2^+$ passed directly through. The solutions containing the dichlorotetraaquochromium(III) species were examined spectrophotometrically between 800 and 300 nm using the 0–0.1 absorbance scale of a Cary 14 recording spectrophotometer. The total chromium content of these solutions was also determined.

Kinetic Measurements.—The $CrCl_2^+$ was generated *in situ* by the reaction of $Co(NH_3)_5Cl^{2+}$ with an excess of chromium(II) and chloride ion in the rapid-flow apparatus. The experimental conditions were adjusted to meet the following criteria: (1) the cobalt(III)–chromium(II) reaction was complete by the time the mixed solution reached the observation tube; (2) the chromium(II)-catalyzed aquation of the $CrCl_2^+$ produced could be followed conveniently by observing the absorbance changes in the 260–245-nm region. This wavelength region was chosen because the molar absorptivities of the $CrCl_2^+$ isomers are quite high[13] ($>10^3$), and therefore very small concentrations of these ions can be readily detected.

Results

The results of the stoichiometric experiments carried out by mixing chromium(II) with an *excess* of $Co(NH_3)_5Cl^{2+}$ in the rapid-flow apparatus, followed

[1] (a) This work was supported by Grant GP-6528 from the National Science Foundation; (b) Fellow of the Alfred P. Sloan Foundation, 1965–1968.

[2] H. Taube, "Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research," Vol. VI, Houston, Texas, 1962, p 7.

[3] D. E. Pennington and A. Haim, *Inorg. Chem.*, **6**, 2138 (1967).

[4] A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

[5] P. V. Manning and R. C. Jarnagin, *J. Phys. Chem.*, **67**, 2884 (1963).

[6] H. Taube and E. L. King, *J. Am. Chem. Soc.*, **76**, 4053 (1954).

[7] H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

[8] Y. T. Chia and E. L. King, *Discussions Faraday Soc.*, **29**, 109 (1960).

[9] A. Haim, *J. Am. Chem. Soc.*, **88**, 2324 (1966).

[10] J. H. Espenson and S. G. Slocum, *Inorg. Chem.*, **6**, 906 (1967).

[11] H. Taube, H. Myers, and R. L. Rich, *J. Am. Chem. Soc.*, **75**, 4118 (1953).

[12] J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).

[13] E. L. King, M. J. M. Woods, and H. S. Gates, *J. Am. Chem. Soc.*, **80**, 5015 (1958).

[14] J. D. Salzman and E. L. King, *Inorg. Chem.*, **6**, 426 (1967).

[15] G. Dulz and N. Sutin, *ibid.*, **2**, 917 (1963).

[16] Because of the insolubility of the salt $[Co(NH_3)_5Cl]Cl_2$ in solutions containing added chloride ion, all stoichiometric and kinetic experiments were carried out with the added chloride ion initially present in the chromium(II) solution.