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

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

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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+}–$Cr(OH_2)_5I^{2+}$, 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 forward reaction in eq 1.

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

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

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 ($k \sim 10^6 M^{-1}\ \text{sec}^{-1}$)[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

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(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.

TABLE I

STOICHIOMETRY OF THE $Co(NH_3)_5Cl^{2+}$–Cr^{2+} REACTION IN THE PRESENCE OF ADDED CHLORIDE ION[a]

$10^2[Co(NH_3)_5Cl^{2+}]$, M	$10^2[Cr^{2+}]$, M	$[Cl^-]$, M[b]	% $CrCl_2^+$ [c]	k_{Cl}/k_0, M^{-1} [d]
1.30	1.09	0.080	1.7	0.22[e]
1.30	1.09	0.16	2.7, 2.8	0.17, 0.18[f]
0.75	0.55	0.50	6.5	0.14[g]

[a] Measurements at 25° by mixing equal volumes of solutions of the specified concentrations in columns 1 and 2. The chloride ion is originally present only in the chromium(II) solution. [b] Final concentration in mixed solution. [c] Calculated from the expression [100 × mmoles of $CrCl_2^+$ recovered]/[mmoles of Cr^{2+} consumed]. Ratio [*cis*-$CrCl_2^+$]/[*trans*-$CrCl_2^+$] = 1.0 ± 0.2. [d] Calculated from the expresssion % $CrCl_2^+/(100 - \%\ CrCl_2^+)\cdot[Cl^-]$. [e] Ionic strength *ca.* 0.16. [f] Ionic strength *ca.* 0.32. [g] Ionic strength *ca.* 0.50.

by separation of the $CrCl_2^+$ produced by ion-exchange chromatography, are presented in Table I.[17] In the absence of added chloride ion, the $Co(NH_3)_5Cl^{2+}$–Cr^{2+} reaction is known[11] to yield $CrCl^{2+}$ quantitatively. In the presence of added chloride ion, the yield of $CrCl^{2+}$ is reduced and $CrCl_2^+$ is produced instead. As shown in column 4 of Table I, the yield of $CrCl_2^+$ increases with increasing chloride ion concentration. The solutions of $CrCl_2^+$ displayed absorption spectra intermediate between those of *cis*- and *trans*-$CrCl_2^+$. From the absorbance at 450 nm (a wavelength where the difference in the molar absorbances between *cis*- and *trans*-$CrCl_2^+$ is relatively large[13,14]) and the total chromium (III) concentration, it was established that the ratio [*cis*-$CrCl_2^+$]/[*trans*-$CrCl_2^+$] produced in the reaction was 1.0 ± 0.2. The significance of the quantity k_{Cl}/k_0 listed in column 5 will be discussed below.

Additional evidence for the formation of *cis*- and *trans*-$CrCl_2^+$ in the reaction of $Co(NH_3)_5Cl^{2+}$ with chromium(II) in the presence of added chloride ion was obtained from the following kinetic measurements. When $Co(NH_3)_5Cl^{2+}$ was mixed in the flow apparatus with an *excess* of chromium(II) in the presence of added chloride ion, changes in absorbance were observed in the 260–245-nm range. Since under the conditions used the $Co(NH_3)_5Cl^{2+}$–Cr^{2+} reaction has a half-life of ~0.1 msec, the observed changes in absorbance clearly demonstrate the formation and decay of an intermediate. Plots of ln $(A_t - A_\infty)$ *vs.* time were linear over 2–3 half-lives, and from the slopes k_p of these plots, second-order rate constants $k = k_p/[Cr^{2+}]$ were calculated. At $[Cr^{2+}] = 5.9 \times 10^{-3}$ M and $[Cl^-] = 0.12$ or 0.50 M, k was 346 ± 20 M^{-1} sec^{-1} (25° and ionic strength 1.0). The observed value 346 M^{-1} sec^{-1} is almost exactly equal to the average of the values[10] 288 and 401 M^{-1} sec for the chromium(II)-catalyzed aquations of *cis*- and *trans*-$CrCl_2^+$, respectively. This rate comparison provides additional evidence for the conclusion that the $CrCl_2^+$ formed in the $Co(NH_3)_5Cl^{2+}$–Cr^{2+} reaction in the presence of added chloride ion consists of a mixture of *cis*- and *trans*-$CrCl_2^+$.[18]

Discussion

The formation of $CrCl^{2+}$ and $CrCl_2^+$ in the $Co(NH_3)_5Cl^{2+}$–Cr^{2+} reaction in the presence of added chloride ion can be readily accounted for on the basis of the parallel inner-sphere reactions represented by eq 3 and 4. According to this scheme, the ratio [$CrCl_2^+$]/[$CrCl^{2+}$] produced in the reaction equals $k_{Cl}\cdot[Cl^-]k_0$. Values of k_{Cl}/k_0 are listed in column 3 of Table I. Although the calculated values of k_{Cl}/k_0 decrease with increasing chloride ion concentration, it must be noted that the measurements in Table I were carried out at variable ionic strength. The decrease in k_{Cl}/k_0 from 0.22 to 0.14 as the ionic strength increases from *ca.* 0.16 to 0.50 M is consistent with the charges of the reactants in eq 3 and 4. The small value of k_{Cl}/k_0 is noteworthy and provides an additional example of the generalization noted previously[2,3] that reactions of substitution-inert oxidants with substitution-labile reductants that proceed *via* an inner-sphere mechanism are rather insensitive to added chloride ion (see also Table VII of ref 3).

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} \xrightarrow[H^+]{k_0} CrCl^{2+} + Co^{2+} + 5NH_4^+ \quad (3)$$

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} + Cl^- \xrightarrow[H^+]{k_{Cl}} CrCl_2^+ + Co^{2+} + 5NH_4^+ \quad (4)$$

Reaction 4 leads to the formation of both *cis*- and *trans*-$CrCl_2^+$. Undoubtedly the detailed mechanism of this reaction features the bridged transition states represented in eq 5 and 6.[19] From the measured product ratio [*cis*-$CrCl_2^+$]/[*trans*-$CrCl_2^+$] we conclude that

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} + Cl^- \rightleftarrows [cis\text{-}(NH_3)_5CoClCrCl^{3+}]^{\ddagger} \longrightarrow cis\text{-}CrCl_2^+ \quad (k_5) \quad (5)$$

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} + Cl^- \rightleftarrows [trans\text{-}(NH_3)_5CoClCrCl^{3+}]^{\ddagger} \longrightarrow trans\text{-}CrCl_2^+ \quad (k_6) \quad (6)$$

$k_5/k_6 = 1.0$, a value significantly smaller than the value 4.0 expected on statistical grounds. This comparison demonstrates that the nonbridging chloride is more effective from the *trans* than from the *cis* position in promoting the electron transfer to the cobalt(III) center.

Entirely analogous conclusions about the effect of added chloride ion and the relative efficiencies of *cis* and *trans* nonbridging chloride ions are reached if the chromium(II)-catalyzed exchange of chlorine atoms between $CrCl^{2+}$ and free chloride ion is interpreted on the basis of the mechanism originally proposed by Taube and King[6] and recently elaborated upon by Espenson and Slocum[10] (eq 7 and 8). The rate constants k_7 and

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[17] Because of an arithmetical error, the yield of $CrCl_2^+$ at $[Cl^-] = 0.50$ M was incorrectly quoted as 3% in our previous work.[3]

[18] It might be argued that the linearity of the ln $(A_t - A_\infty)$ *vs.* time plots is incompatible with the conclusion that a mixture of isomers (*cis*- and *trans*-$CrCl_2^+$) of different reactivity toward chromium(II) is produced in the $Co(NH_3)_5Cl^{2+}$–Cr^{2+}–Cl^- reaction. However, at 260 nm, an isosbestic point for *cis*- and *trans*-$CrCl_2^+$, a calculated plot of ln $(A_t - A_\infty)$ *vs.* time for the chromium(II)-catalyzed aquation of an equimolar mixture of the two isomers is essentially linear during 2–3 half-lives and yields an apparent second-order rate constant of 342 M^{-1} sec^{-1}. At 250 nm, where the molar absorptivities of $CrCl^{2+}$, *cis*-$CrCl_2^+$, and *trans*-$CrCl_2^-$ are ~10^2, ~1.1×10^3, and ~1.7×10^3, respectively, the ln $(A_t - A_\infty)$ *vs.* time plot is linear for 3 half-lives, and yields a rate constant of 352 M^{-1} sec^{-1}.

[19] The designations *cis* and *trans* for the transition states in eq 5 and 6 refer to the geometrical configuration of the chloride ions around the chromium.

$$CrCl^{2+} + Cr^{2+} + Cl^- \rightleftharpoons cis\text{-}CrCl_2^+ + Cr^{2+} \qquad (k_7) \quad (7)$$

$$CrCl^{2+} + Cr^{2+} + Cl^- \rightleftharpoons trans\text{-}CrCl_2^+ + Cr^{2+} \qquad (k_8) \quad (8)$$

k_8 have the values 0.44 and 0.56 M^{-2} sec^{-1} at 0°.[20] Again the ratio of $k_7/k_8 = 0.79$ is significantly smaller than the statistically expected value of 4.0. Moreover, a comparison of the value $k_7 + k_8 = 1.0\ M^{-2}$ sec^{-1} (0°) with the value $k_9 = 9\ M^{-1}$ sec^{-1} (0°) for reaction 9[21] illustrates once more the small effect of added chloride ion on the rate of inner-sphere reactions.

$$*CrCl^{2+} + Cr^{2+} \rightleftharpoons CrCl^{2+} + *Cr^{2+} \qquad (k_9) \quad (9)$$

It is instructive to recast the chloride ion effects on the electron-transfer reactions considered above in the form of equilibrium constants involving transition states. Calculations have been previously carried out for acid dissociation constants[22,23] and can be generalized to many other formal reactions of transition states.[24] As an example, it can be seen that the proper combination of eq 10, 11, and 12 leads to eq 13 and a calculated value of $Q_{13} = 5.8 \times 10^6\ M^{-1}$.

$$Co(NH_3)_5OH_2^{3+} + Cr^{2+} \rightleftharpoons [(NH_3)_5Co(OH_2)Cr^{5+}]^{\ddagger} \qquad (k_{10} = 0.50\ M^{-1}\ sec^{-1}) \quad (10)$$

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} \rightleftharpoons [(NH_3)_5CoClCr^{4+}]^{\ddagger} \qquad (k_{11} = 2.6 \times 10^6\ M^{-1}\ sec^{-1}) \quad (11)$$

$$Co(NH_3)_5OH_2^{3+} + Cl^- \rightleftharpoons Co(NH_3)_5Cl^{2+} + H_2O \qquad (Q_{12} = 1.11\ M^{-1}) \quad (12)$$

$$[(NH_3)_5Co(OH_2)Cr^{5+}]^{\ddagger} + Cl^- \rightleftharpoons [(NH_3)_5CoClCr^{4+}]^{\ddagger} + H_2O \quad (13)$$

Calculated values of Q for the formal reactions of the transition states of interest in the present note are summarized in Table II. Although no new information is obtained by recasting the chloride ion effects in terms of the equilibrium constants listed in Table II, the approach provides a useful summary of these effects. For example, comparisons of eq A with B and C and of eq D with E and F clearly illustrate the enormous difference between the effect of chloride ion in bridging as compared to nonbridging positions. Reactions A and D feature the substitution of a bridging water by chloride ion, and are seen to be extremely favorable ($Q > 10^5$). In contrast, reactions B, C, E, and F, which feature the substitution of a *cis* or *trans* nonbridging water by chloride ion, are relatively unfavorable (Q = 0.05–0.1). Moreover, the values Q = 1.0 and 0.8 for reactions G and H, respectively, when compared with the statistically expected value of 4.0, clearly demonstrate the increased stability of the transition states containing *trans* chloride ions. Interestingly, an entirely similar observation regarding the relative stabilities of *cis* and *trans* isomers was previously made for the $CrCl_2^+$ system.[13,14]

TABLE II

FORMAL EQUILIBRIUM CONSTANTS FOR SUBSTITUTION OF WATER BY CHLORIDE ION IN CHROMIUM-CONTAINING TRANSITION STATES

	Reactions	Q, M^{-1} [a]	Ref
A.	$[(NH_3)_5Co(OH_2)Cr^{5+}]^{\ddagger} + Cl^- \rightleftharpoons [(NH_3)_5CoClCr^{4+}]^{\ddagger} + H_2O$	5.8×10^6	*b, c, d*
B.	$[(NH_3)_5CoClCr^{4+}]^{\ddagger} + Cl^- \rightleftharpoons [cis\text{-}(NH_3)_5CoClCrCl^{3+}]^{\ddagger} + H_2O$	0.1	This work
C.	$[(NH_3)_5CoClCr^{4+}]^{\ddagger} + Cl^- \rightleftharpoons [trans\text{-}(NH_3)_5CoClCrCl^{3+}]^{\ddagger} + H_2O$	0.1	This work
D.	$[(H_2O)_5Cr(OH_2)Cr^{5+}]^{\ddagger} + Cl^- \rightleftharpoons [(H_2O)_5CrClCr^{4+}]^{\ddagger} + H_2O$	$>10^5$	*e, f, g*
E.	$[(H_2O)_5CrClCr^{4+}]^{\ddagger} + Cl^- \rightleftharpoons [cis\text{-}(H_2O)_5CrClCrCl^{3+}]^{\ddagger} + H_2O$	0.05	*f, h, i*
F.	$[(H_2O)_5CrClCr^{4+}]^{\ddagger} + Cl^- \rightleftharpoons [trans\text{-}(H_2O)_5CrClCrCl^{3+}]^{\ddagger} + H_2O$	0.06	*f, h, i*
G.	$[trans\text{-}(NH_3)_5CoClCrCl^{3+}]^{\ddagger} \rightleftharpoons [cis\text{-}(NH_3)_5CoClCrCl^{3+}]^{\ddagger}$	1.0	This work
H.	$[trans\text{-}(H_2O)_5CrClCrCl^{3+}]^{\ddagger} \rightleftharpoons [cis\text{-}(H_2O)_5CrClCrCl^{3+}]^{\ddagger}$	0.8	*f, h, i*

[a] Values for reactions A–C and G at 25°. Values for reactions D–F and H at 0°. [b] A. M. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **81**, 1288 (1959). [c] Reference 12. [d] D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967). [e] A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954). [f] Reference 21. [g] C. F. Hale and E. L. King, *J. Phys. Chem.*, **71**, 1779 (1967). [h] Reference 10. [i] Reference 14.

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Reaction of Chlorine Monofluoride with Some Group VI Elements and Derivatives

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As a fluorinating agent, chlorine monofluoride has been placed approximately below F_2, ClF_3, BrF_5, and IF_7 in reactivity.[1,2] The available information for such an assignment is mostly qualitative. For example, relatively little is known about the reactivity of chlorine monofluoride with group VI elements. Sulfur is said to react slowly and without flame, but no products are specified.[3] With SF_4 at 350°, chlorine monofluoride is said to react as a chlorofluorinating agent to yield SF_5Cl.[4]

Acting as a moderate fluorinating agent, chlorine monofluoride should have a number of attractive synthesis applications. This paper describes the investigation of reactions between chlorine monofluoride

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