

Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. X. Structure and Reactivity of Ammineaquadichloridochromium(III) Complexes

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Four compounds with the stoichiometric composition: $[\text{Cr}(\text{NH}_3)_x(\text{OH}_2)_{4-x}\text{Cl}_2]\text{Cl}$ ($x = \text{mer-3, cis-2, trans-2}$ and 1) have been investigated. They all have been shown to have a *trans* dichlorido configuration. In acid solution both isomerization to *cis* dichlorido isomers with unchanged ammine configuration and also chloride ligand substitution take place. The kinetics of the latter process have been investigated by using a chloride ion sensitive electrode, and data at 50–80 °C, 0.25–1.00 M H^+ for a 1.00 M $(\text{Na,H})\text{ClO}_4$ medium are reported. In combination with previous data for hydrolysis of the ammineaquachromium(III) isomers, a common pattern has been established for the effect of coordinated water and ammonia in *cis* position to the reacting ligand for the three series of complexes.

Isomerization of *cis*- and *trans*-tetraaquadichloridochromium(III) occurs in acid aqueous solution in addition to the formation of pentaquachloridochromium(III).^{1,2} This contrasts the reported behaviour both of the pair of tetraamminedichloridochromium(III) complexes,^{3,4} and of a pair of aminetriaquadichloridochromium(III) complexes.⁵ In none of these latter cases was isomerization detected. Dichloridochromium(III) species derived from *mer*-triammine-^{6,7} and *cis*-⁸ and *trans*-diamminechromium(III)⁹ have been prepared, but these compounds have apparently not been investigated kinetically. Information on stereochemical changes of chromium(III) complexes is very limited, and therefore this study was undertaken to find whether

these complexes would conform to the picture established for the tetraqua- or the tetraamminechromium(III) species.

EXPERIMENTAL

Chemicals. *trans*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$,¹⁰ *trans*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{ClO}_4$,¹⁰ *cis*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$,⁴ *cis*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{ClO}_4$,⁴ *mer*- $[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)\text{Cl}_2]\text{Cl}$,^{6,7} *cis*- $[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_2\text{Cl}_2]\text{Cl}$,⁸ and *trans*- $[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_2\text{Cl}_2]\text{Cl}$,⁹ where all the prefixes relate to the ammine configuration, were prepared by literature methods. Crude $[\text{Cr}(\text{NH}_3)(\text{OH}_2)_3\text{Cl}_2]\text{Cl}$ was prepared by vacuum evaporation to dryness of a solution of $[\text{Cr}(\text{NH}_3)(\text{OH}_2)_5]^{3+}$ in 4 M hydrochloric acid at 50 °C.¹¹ The solid substance thus obtained was recrystallized twice by the method described for *trans*- $[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$.¹² The sources of the other chemicals employed have been described earlier.¹³

Ion exchange separations of this type of complexes,² *methods of analyses*¹³ and *spectrophotometric measurements*² have all been described earlier.

X-Ray powder photographs were taken with $\text{CuK}\alpha$ radiation using a focusing camera of the Guinier type.

Kinetic measurements. All the reactions studied in this paper proceed with the release of coordinated chloride ions. The progress of the reactions could therefore conveniently be followed potentiometrically. The measurements were carried out directly in the reacting solutions using a silver/silver chloride

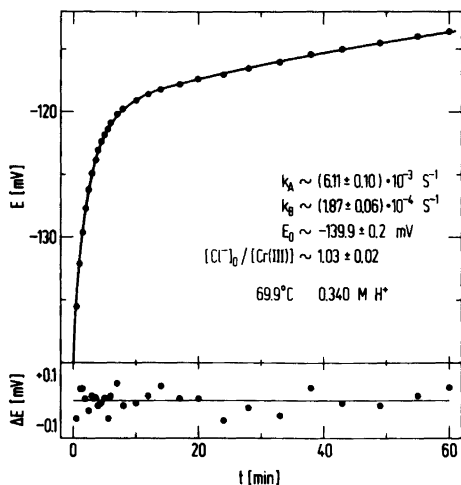


Fig. 1. Kinetic experiment started by dissolving $trans\text{-}[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ in 1 M perchlorate solution. Upper part: Experimental (●) and calculated (—) time dependence of the potential. The solid curve is calculated from the parameter values shown on the figure.

Lower part: Differences between experimental and calculated potentials.

electrode, prepared in a way which assured rapid response,¹⁴ in combination with either a Radiometer PHM 52 digital pH-meter or a Varian G-2000 strip-chart recorder. The need to raise the temperature up to 80 °C and the requirement for accurate measurements of small potential differences place severe limitations on usable reference electrodes. Finally a silver/silver chloride electrode in the reaction medium, made ~1 mM in chloride ions, and separated from the reaction solution by a porous glass disc, was employed.

The kinetic experiments were all started by the addition of a suitable amount of the solid chro-

Table 1. Kinetic data for the process: $trans\text{-}[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+ \rightarrow trans\text{-}[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}]^{2+} + \text{Cl}^-$ in 1.00 M (Na,H)ClO₄.

| $10^4 k$ (45 °C) [s ⁻¹] | E [kJ mol ⁻¹] | Ref. |
|--|--------------------------------|----------------|
| 4.8 ± 0.1 | 90.4 ± 1.3 | 3 ^a |
| 4.6 ± 0.2 | 91.4 ± 1.6 | b |

^a Spectrophotometric data at 45–55 °C, 0.20–1.00 M H⁺. ^b This work. Potentiometric data at 50–80 °C, 0.25–1.00 M H⁺.

Table 2. Kinetic data for the process: $cis\text{-}[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+ \rightarrow cis\text{-}[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}]^{2+} + \text{Cl}^-$.

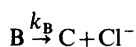
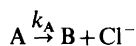
| $10^5 k$ (25 °C) [s ⁻¹] | E [kJ mol ⁻¹] | Ref. |
|--|--------------------------------|----------------|
| 33.0 ± 1.5 | 87.0 ± 2.1 | 4 ^a |
| 21.2 ± 0.9 | 92.4 ± 1.1 | b |

^a Spectrophotometric data at 20–45 °C, 0.01–0.40 M H⁺ in 0.40 M (Na,H)NO₃. ^b This work. Potentiometric data at 30–70 °C, 0.33–1.00 M H⁺ in 1.00 M (Na,H)-ClO₄.

mium(III) compound as the chloride or the perchlorate salt to the thermostated reaction medium. The results of a typical experiment are shown in Fig. 1. To ascertain the validity of the present experimental approach, the first stage of the hydrolysis of $trans$ -tetraamminedichloridochromium(III) was reexamined. This process has earlier been investigated spectrophotometrically,³ and a comparison is given in Table 1. The agreement is satisfactory and supports the use of the direct potentiometric method for the study of the present reactions.

cis -Tetraamminedichloridochromium(III) was also re-examined analogously in order to obtain data for a 1.00 M perchlorate medium. The results for this reaction are given in Table 2. They are slightly different from those obtained earlier by a spectrophotometric method, but this is not unexpected since the reaction medium is changed.

Method of calculation. When chloride ions are released in a two stage process:



and $k_A \neq k_B$, the following expression, for an experiment started without B and C, is valid for the chloride ion concentration at time t :

$$[\text{Cl}^-]_t = [\text{Cl}^-]_0 + [\text{A}]_0 \left\{ 2 + \frac{2k_B - k_A}{k_A - k_B} \exp(-k_A t) - \frac{k_A}{k_A - k_B} \exp(-k_B t) \right\}$$

and the potential of a chloride sensitive electrode is given by:

$$E_t = E_0 + \frac{RT}{F} \ln \frac{[\text{Cl}^-]_t}{[\text{Cl}^-]_0}$$

The experimental points $E(t)$ were approximated by a curve calculated using these expressions from the four parameters: k_A , k_B , E_0 and $[\text{Cl}^-]_0/[\text{A}]_0$, estimated by minimization of:

$$\sum_t (E(t) - E_t)^2 / (\sigma_E^2 + \left(\frac{dE}{dt}\right)^2 \sigma_t^2)$$

where σ_E^2 and σ_t^2 are the variances of potential and time measurements, respectively. This proceeded without difficulties, cf. Fig. 1, and is a convenient way to overcome the difficulties encountered in an analytical estimation of $[\text{Cl}^-]_0$. The further calculations to yield activation parameters were carried out essentially as described previously.²

RESULTS AND DISCUSSION

Solid dichloridochromium(III) compounds have been prepared with various combinations of ammonia and water ligands at the four remaining coordination positions. Only one of the two possible tetraaquadichloridochromium(III) isomers has been crystallized, and this is known to have the *trans* dichlorido configuration.^{15,16} Tetraamminedichloridochromium(III) may be crystallized as salts of various anions,^{3,4,10} and although no direct structural investigations have apparently been carried out on any of these compounds the existence and properties of both isomers have allowed unambiguous structural conclusions to be drawn.

Four solid dichlorido derivatives of triammine-, diammine- and monoamminechromium(III) have so far been obtained, but these ammineaquadichloridochromium(III) ions are structurally less well characterized than the dichlorido derivatives of tetraammine- and tetraaquachromium(III). Mercury(II)-accelerated chloride ligand substitution yields usually for this type of complexes products in which the major component has an unchanged ammine configuration. For the dichloridochro-

mium(III) complexes dealt with here mercury(II) generates pure *mer*-triamminetriaquachromium(III) from the dichlorido compound prepared from triamminediperoxochromium(IV)^{6,7} and pure *cis*- and *trans*-diamminetetraaquachromium(III) from the two diammines prepared from "Rhodoschromium(III) chloride"⁸ and "Reinecke salt",⁹ respectively. Structural investigations on the three starting materials show that these also have a *mer*-triammine¹⁷ and a *cis*-¹⁸ and a *trans*-diammine¹⁹ configuration. Therefore, since the three compounds investigated here are both generated from and yield products with identical ammine configurations, these configurations most likely also persist in the solid ammineaquadichloridochromium(III) chlorides.

Information on the configuration of the two chloride ligands is less easily obtained. For the *mer* triammine and *trans* diammine derivatives both a *trans* and a *cis* dichlorido configuration is possible whereas for both the *cis* diammine and the monoammine two *cis* and one *trans* isomer may exist.

The isomeric pairs of both the tetraammine- and the tetraaquadichloridochromium(III) ions can be separated by ion exchange chromatography,² and in both cases the *trans* isomer is eluted first. Similar fractionation experiments on freshly prepared solutions of the other four monovalent ammineaquadichlorido ions do not reveal the existence of separable isomers in these solutions, judged from the visible absorption spectra of successive column eluates. The spectral characteristics are given in Table 3.

Solutions of these dichlorido ions aged for 1–2 half-lives with respect to substitution of the first chloride ligand exhibit, however, an elution behaviour, for the band of monovalent species, which is different: For all the four ions in question only the first fractions of the band of monovalent species contain a species with an absorption spectrum identical to that of the freshly prepared

Table 3. Spectral characteristics of solutions of *trans*-dichlorido complexes prepared and purified as described in the text and diluted with perchloric acid to yield a 0.5 M perchloric acid solution.

| Complex | λ_1 max [nm] | ϵ_1 max [l mol ⁻¹ cm ⁻¹] | λ_2 max [nm] | ϵ_2 max [l mol ⁻¹ cm ⁻¹] | ϵ_1 max/ ϵ_2 max |
|---|-------------------------|---|-------------------------|---|------------------------------------|
| <i>mer</i> -[Cr(NH ₃) ₃ (H ₂ O)Cl ₂] ⁺ | 597 | 25.9 | 409 | 27.1 | 0.956 |
| <i>cis</i> -[Cr(NH ₃) ₂ (H ₂ O) ₂ Cl ₂] ⁺ | 604 | 33.8 | 419 | 24.8 | 1.363 |
| <i>trans</i> -[Cr(NH ₃) ₂ (H ₂ O) ₂ Cl ₂] ⁺ | 583 | 23.9 | 421 | 26.4 | 0.905 |
| [Cr(NH ₃)(H ₂ O) ₃ Cl ₂] ⁺ | 612 | 31.7 | 434 | 23.4 | 1.355 |

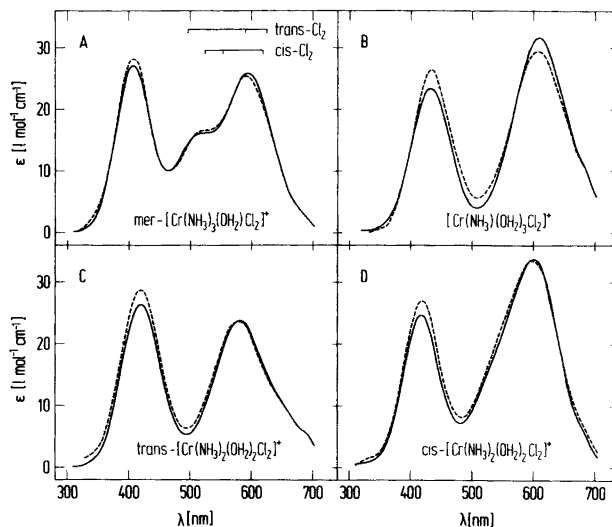


Fig. 2. Visible absorption spectra of ammineaquadichloridochromium(III) complexes. Solid curves: Pure isomers. Broken curves: Last fraction of dichlorido species after ageing in solution (see the text).

solutions. The latter fractions have a different absorption spectrum. This is shown in Fig. 2A–D. Treatment of the eluates with mercury(II) reveal an unchanged ammine configuration, and therefore the observed difference in elution behaviour is caused by a change in the configuration of the remaining ligands. The elution behaviour of these fresh and aged solutions can be compared with that of the isomeric tetraammine- and tetraaquadichloridochromium(III) isomers. This indicates firstly that the four solid ammineaquachromium(III) salts contain *trans* dichlorido isomers, and secondly that these in aqueous solution slowly isomerize to form *cis* dichlorido isomers.

Additional evidence in favour of a *trans* dichlorido configuration of the solid ammineaquadichloridochromium(III) chlorides comes from absorption spectra and X-ray powder diffraction photographs:

Fig. 2A shows calculated band component positions, using the model and the parameters described in Ref. 20, for the *cis* and *trans* dichlorido isomers derived from the *mer* triammine. Comparisons with the observed absorption spectrum clearly support the assignment of a *trans* dichlorido configuration to the cation of solid *mer*-triammineaquadichloridochromium(III) chloride. For the remaining dichlorido complexes this approach yields no additional information, since the calculated band component positions differ too little to be of value in

this respect.

Empirically the same pattern of variation of the intensities of the first and second spin-allowed absorption band is observed for all the pairs of dichlorido isomers: The second band shows an increase in intensity and the first a decrease in intensity on the lower wave-length side when going from the assumed pure *trans* dichlorido isomers to the mixtures of *cis* and *trans* isomers. This is similar to the variation observed from *trans*- to *cis*-tetraammine- and -tetraaquadichloridochromium(III),^{3,4,2} and support the assumption that *cis* dichlorido isomers are formed in solution from the *trans* isomers.

Significant similarities exist between the so-called “dichrochloride” and the solid chloride salts of the dichlorido derivatives of the *mer* triammine and the *cis* diammine. This can be seen both from the marked red–blue-green dichroism of all these three substances and also from the very similar X-ray powder diffraction photographs. “Dichrochloride” is known from a crystal structure analysis to be *mer*-triammineaqua-*trans*-dichloridocobalt(III) chloride,²¹ and this again supports the configurational assignments.

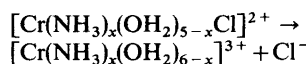
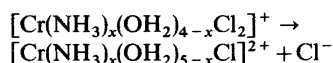
Kinetic investigations of the reactions of these dichlorido complexes are obviously complicated by the concurrent isomerization and loss of chloride ligand, in particular since the generated *cis* isomers

Table 4. Rate constants at 70 °C and activation energies for the acid independent reactions of some *trans*-dichloridochromium(III) complexes in aqueous 1.00 M (Na,H)ClO₄ solution.

| Complex | 10 ³ <i>k</i> (70 °C) ^a [s ⁻¹] | <i>E</i> ^a [kJ mol ⁻¹] |
|---|--|--|
| <i>mer</i> -[Cr(NH ₃) ₃ (OH ₂)Cl ₂] ⁺ | 7.45 ± 0.14 | 102.3 ± 1.3 |
| <i>cis</i> -[Cr(NH ₃) ₂ (OH ₂) ₂ Cl ₂] ⁺ | 9.9 ± 0.3 | 96.2 ± 2.1 |
| <i>trans</i> -[Cr(NH ₃) ₂ (OH ₂) ₂ Cl ₂] ⁺ | 4.39 ± 0.05 | 96.5 ± 1.1 |
| [Cr(NH ₃)(OH ₂) ₃ Cl ₂] ⁺ | 7.2 ± 0.3 ^b | 96.2 ± 2.5 ^b |

^a Data based on 15–20 experiments for each complex, covering the temperature and hydrogen ion concentration ranges 50–80 °C and 0.25–1.00 M H⁺, respectively. For this range of hydrogen ion concentrations, the reaction rate constants were independent of the hydrogen ion concentration. ^b These data are at variance with an earlier investigation in 1 M perchlorate solution of a complex said to be aminetriaqua-*trans*-dichloridochromium(III).⁵ From the data in Ref. 5 it may be calculated that *k* (70 °C) ~ (4.2 ± 0.3) 10⁻³ s⁻¹ and *E* ~ 84.5 ± 0.9 kJ mol⁻¹. Two absorption spectra of this species given in Ref. 5 do not agree with each other, nor do they agree with Fig. 2B of this paper, but both may be expressed as a linear combination of this latter spectrum and that of the *cis* isomer in Ref. 5. From the reported ε₁/ε₂ ratios *trans* isomer contents in the said *trans* isomer of Ref. 5 of about 77% and 51% are calculated from Figs. 1 and 2B in Ref. 5, respectively. This explains the discrepancy between the present data and those earlier reported.

have not yet been obtained in a pure state. It has earlier been demonstrated that spectrophotometric measurements are less readily interpreted when components of unknown spectral characteristics are present.¹ Therefore the kinetic investigations in this work were based upon measurements of generated chloride ions. A series of experiments were carried out using a 1.00 M perchlorate medium, over a range of temperature and hydrogen ion concentration of 50–80 °C and 0.25–1.00 M H⁺, respectively. All the results could be interpreted by the simplified reaction scheme:



which is additional evidence in favour of the presence of only small amounts of *cis* dichlorido isomers. A summary of the data thus obtained for the first step is given in Table 4.

The absence of noticeable amounts of *cis* isomers, indicated by the chromatographic experiments, does not preclude the possibility that these isomers are important for the observed release of coordinated chloride ions. Comparisons with the known reactivities of other chloridochromium(III) complexes, *cf.* Table 5, indicate that provided at least one of the chloride ligands in the generated *cis* dichlorido isomer is in *trans* position to coordinated ammonia this complex is expected to

Table 5. Kinetic parameters for hydrolysis of chloridochromium(III) complexes in 1 M perchlorate solution.

| Complex | 10 ⁵ <i>k</i> (25 °C) ^b [s ⁻¹] | Δ <i>H</i> [†] [kJ mol ⁻¹] | Δ <i>S</i> ^{†b} [J K ⁻¹ mol ⁻¹] | Ref. |
|---|---|--|--|-----------------|
| <i>trans</i> -[Cr(NH ₃) ₄ Cl ₂] ⁺ | 4.5 ± 0.3 | 88.9 ± 1.2 | -29 ± 4 | 3, ^a |
| <i>cis</i> -[Cr(NH ₃) ₄ Cl ₂] ⁺ | 21.2 ± 0.9 | 89.7 ± 1.1 | -14 ± 3 | ^a |
| <i>trans</i> -[Cr(OH ₂) ₄ Cl ₂] ⁺ | 4.53 ± 0.11 | 95.7 ± 1.4 | -7 ± 4 | 2 |
| <i>cis</i> -[Cr(OH ₂) ₄ Cl ₂] ⁺ | 1.53 ± 0.15 | 101 ± 5 | +1 ± 17 | 2 |
| <i>mer</i> -[Cr(NH ₃) ₃ (OH ₂)Cl ₂] ⁺ | 3.31 ± 0.21 | 99.5 ± 1.3 | +4 ± 4 | ^a |
| <i>cis</i> -[Cr(NH ₃) ₂ (OH ₂) ₂ Cl ₂] ⁺ | 6.1 ± 0.6 | 93.4 ± 2.1 | -11 ± 6 | ^a |
| <i>trans</i> -[Cr(NH ₃) ₂ (OH ₂) ₂ Cl ₂] ⁺ | 2.65 ± 0.16 | 93.7 ± 1.1 | -17 ± 3 | ^a |
| [Cr(NH ₃)(OH ₂) ₃ Cl ₂] ⁺ | 4.5 ± 0.5 | 93.4 ± 2.5 | -14 ± 7 | ^a |
| [Cr(NH ₃) ₅ Cl] ^{2+c} | 0.98 ± 0.03 | 90.4 ± 1.3 | -38 ± 4 | 22, 23, 24 |
| [Cr(OH ₂) ₅ Cl] ²⁺ | 0.0277 | 101.7 ± 0.8 | -30 ± 2 | 25 |

^a This work. ^b Rate constants and activation entropies are not corrected statistically for the dichlorido complexes (*R* ln 2 ~ 5.8 J K⁻¹ mol⁻¹). ^c 0.1 M perchlorate solution.

hydrolyze so fast that it will not accumulate in significant quantities. In this case the observed rate constant will be a mixture of that for the direct chloride release path and that for the isomerization path which is followed by the rapid chloride ligand release. For the *cis* dichlorido isomers derived from both the *mer* triammine and the *cis* diammine one chloride ligand is always in *trans* position to coordinated ammonia, for the monoammine derivative such a configuration is present in one of the *cis* dichlorido isomers, whereas for the *cis* dichlorido derivative of the *trans* diammine the possibility of a chloride ligand in *trans* position to an ammonia ligand does not exist. Consequently, except for the *trans* diammine derivative, the possibility of significant contributions from an isomerization reaction to the observed rate of chloride ligand release cannot be eliminated.

Both the ΔH^\ddagger and the ΔS^\ddagger values of the series of reactions of the *trans* dichlorido isomers increase almost linearly as functions of the number of water ligands in the complex, if the reactivity parameters of the *trans* dichlorido isomer derived from the *mer* triammine are disregarded. For this latter complex positive deviations from the linear correlation of about $+9 \text{ kJ mol}^{-1}$ and $+26 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, are found. The activation parameters for the isomerization reaction of the *trans*-tetraaquadichloridochromium(III) ion are about 18 kJ mol^{-1} and $57 \text{ J K}^{-1} \text{ mol}^{-1}$ more positive than those for the hydrolysis reaction.² The result of a comparison between these two sets of values is therefore a strong indication of a significant contribution from an isomerization path to the observed chloride release for the *mer* triammine derivative, in contrast

to the remaining data, which correlate well with those for the tetraammine and the tetraaqua complexes, for which the reported values are those for the direct chloride release path. Therefore the reactivity parameters of the dichlorido derivatives of both the *cis*- and the *trans* diammine and the monoammine do not seem to be influenced significantly by isomerization reactions.

In Table 6 the influences of the systematic variation of the four *cis* ligands from tetraammine to tetraaqua are shown for the three types of reaction where all the possible combinations of water and ammonia ligands are known. In all the three series of reactions the effect of this variation of the *cis* ligands is small, amounting usually to less than a factor of two on the reaction rate constants. Within this range, however, the variation in rate constants as function of the *cis* ligands is rather consistent: If the rate constants are labeled according to the number (1, 2, 3 or 4) and configuration (*cis* or *trans*) of ammonia ligands in the four *cis* positions to the reacting ligand which may be thought of as a square planar complex the following series of inequalities:

$$k_4 < k_3 \sim k_1 < k_{2c}$$

and: $k_3 \sim k_1 > k_{2t}$

for the kinetic *cis* effect of water compared to ammonia holds through the three series of complexes. In view of the differences in both leaving ligands and *trans* ligands of the series of reactions upon which this pattern is based, the consistency of the *cis* effect is somewhat surprising and may be taken as evidence in favour of the hypothesis

Table 6. Statistically corrected rate constants for some reactions of the type: $[\text{Cr}(\text{cis})_4(\text{trans})\text{X}] + \text{H}_2\text{O} \rightarrow [\text{Cr}(\text{cis})_4(\text{trans})(\text{OH}_2)] + \text{X}$.

| (<i>cis</i>) ₄ | $10^6 k (70^\circ\text{C})^a$ [s ⁻¹] | $10^6 k (70^\circ\text{C})^a$ [s ⁻¹] | $10^3 k (70^\circ\text{C})^b$ [s ⁻¹] |
|---|---|---|---|
| (NH ₃) ₄ | 8.0 ± 0.2 | 0.0 ± 0.5 | 2.89 ± 0.06 |
| (NH ₃) ₃ (OH ₂) | 11.8 ± 0.2 | 1.7 ± 0.3 | 3.72 ± 0.07 |
| <i>cis</i> -(NH ₃) ₂ (OH ₂) ₂ | 12.1 ± 0.3 | 2.53 ± 0.10 | 4.45 ± 0.14 |
| <i>trans</i> -(NH ₃) ₂ (OH ₂) ₂ | 11.1 ± 0.2 | 0.5 ± 0.4 | 2.19 ± 0.03 |
| (NH ₃)(OH ₂) ₃ | 11.8 ± 0.2 | 1.69 ± 0.04 | 3.62 ± 0.13 |
| (OH ₂) ₄ | 8.75 ± 0.15 | 1.108 ± 0.011 | 4.1 ± 0.3 |
| <i>trans</i> | NH ₃ | OH ₂ | Cl ⁻ |
| X | NH ₃ | NH ₃ | Cl ⁻ |

^a Ref. 26. ^b This work, Tables 1 and 4, and Ref. 2.

earlier advanced for the interactions between the leaving ligand and the *cis* ligands,²⁷ namely that these interactions are not very different in the transition state and the ground state for the present type of complexes.

With the work described here and that in the literature the whole series of ammineaqua-*trans*-dichloridochromium(III) complexes has been investigated kinetically. Isomerization reactions are only observed when water is present in the first coordination sphere and this supports the view earlier advanced that configurational changes of such simple chromium(III) complexes occur as the result of solvent exchange.^{2,28}

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