Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. XIII. Water Exchange of 
*mer*-Triamminetriaquaquea- and Amminepentaaquachromium(III). 
Kinetic *cis* Effect of Ammonia vs. Water

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The rate of water exchange of *mer*-triamminetriquaqua- and of amminepentaaquachromium(III) in an acid 1 M perchlorate medium has been investigated. The kinetics of both systems are characterized by two first order processes for which the rate constants at 25 °C are:

\[
\begin{align*}
\text{mer}-[\text{Cr(NH}_3)_3(\text{OH}_2)_2]\text{Cl}^{3+} : & (7.6 \pm 1.0) \times 10^{-5} \text{ s}^{-1}, \\
(1.23 \pm 0.05) \times 10^{-5} \text{ s}^{-1}; & \\
[\text{Cr(NH}_3)_3(\text{OH}_2)_2]\text{Cl}^{3+} : & (2.8 \pm 0.4) \times 10^{-5} \text{ s}^{-1}, \\
(0.449 \pm 0.014) \times 10^{-5} \text{ s}^{-1}. &
\end{align*}
\]

The two types of water ligands in both complexes are exchanged by processes which are largely stereoretentive, and the two larger rate constants are both associated with the reactivity of the water ligand *trans* to an ammonia ligand. Common features in the reactivity pattern for the exchange of water ligands in amminepentaaquachromium(III) complexes have been established and can be rationalized on the basis of an associative interchange mechanisms.

Few systematic studies of the effect of non-reacting ligands on the reactivity of transition metal complexes have been reported. We have earlier studied the ammonia ligand aquation of the isomeric amminepentaaquachromium(III) complexes in order to establish data for the kinetic *cis* and *trans* effect of coordinated ammonia vs. water.\(^1\) For this system it was not possible, however, to obtain well-defined rate constants for some of the slower reactions because of an unfavourable competition between slow and faster reactions. The water exchange reactions of the same set of complexes are free from this complication. They can all be studied experimentally and the present work describes kinetic water exchange studies of *mer*-triamminetriquaqua- and of amminepentaaquachromium(III) which in combination with earlier studies\(^2,3\) completes our work on this series of complexes.

**EXPERIMENTAL**

Chemicals. *mer*-Cr(NH\(_3\))\(_3\)(OH\(_2\))Cl\(_2\) and Cs[Cr(NH\(_3\))\(_3\)(OH\(_2\))]\(_2\)SO\(_4\)\(_2\) \(6\)H\(_2\)O\(^6,7\) were prepared by literature methods. Ba(tos)\(_2\) \(^*\) was prepared from warm aqueous solutions of Ba(OH)\(_2\) + 2H tos. The sources of other chemicals have been described earlier.\(^2,3\)

Preparation of oxygen-18 labelled mer-triamminetriaquaquea(III). This cation was labelled with oxygen-18 enriched water by Ag(I) accelerated chloride ligand removal from the mer-triamminetriaquea-trans-dichloridochromium(III) cation followed by equilibration in oxygen-18 enriched water, essentially as described for *cis*-diamminetriaquaquea(III), at method A in Ref. 3. This method was used for experiments 1 - 4 and 6 in Table 1. Experiment 5 shows an attempt to label the water ligand *trans* to ammonia stereospecifically by method C of Ref. 3. The \(\delta_{1}/\delta_{2}\)

\(^*\) tos = p-toluenesulfonate = p-CH\(_3\)C\(_6\)H\(_4\)SO\(_3\)\(_-\).
ratio was slightly larger and, as found out for cis-diaminotetraaquachromium(III), some water ligand isomerization takes place during the purification procedure so that further experiments of this type were not carried out.

Preparation of oxygen-18 labelled amminepentaaqua chromium(III). A mixture of 150 mg Cs[Cr(NH₃)₃(OH₂)₂][SO₄]₂·6H₂O + 40 mg tosH + 250 mg Ba(tos)₂ was equilibrated in 1.0 ml of oxygen-18 enriched water at 60°C for 50 min after which excess water was removed by sublimation in vacuum. The remaining solid was treated with 5 ml 0.01 M HClO₄ and BaSO₄ filtered off. The resulting solution which in addition to the desired [Cr(NH₃)(OH₂)₂]⁺³ mainly contains Ba²⁺ and small amounts of sulphato- and tosylatochromium(III) complexes was purified by ion exchange chromatography as described in detail in Ref. 2. The monoamminepentaaqua ion solution prepared in this way was the basis for experiments 1 and 2 in Table 2. It was also attempted to label a larger fraction of the ‘fast’ water ligand site by reducing the equilibration time. Experiments 3 and 4 show two such attempts, which significantly reduces the uncertainty of the kₘ rate constant.

Kinetic measurements, methods of analyses, spectrophotometric measurements, mass spectrometric measurements and the method of calculation were essentially as described previously.²⁻³

RESULTS AND DISCUSSION

Exchange of oxygen-18 labelled water from mer-triaminotetraaquachromium(III) takes place with retention of the ammine configuration. For both this cation and amminepentaaqua chromium(III) the exchange follows a sum of two exponential functions, i.e.: ¹⁸O] = [¹⁸O]₀ + [Cr(III)] × \[δ₁[1-exp(-k₁t)] + δ₂[1-exp(-k₂t)]\]  

(1)

Table 1. Summary of kinetic data for water exchange in mer-[Cr(NH₃)₃(OH₂)₂]⁺³ in 0.50 M HClO₄ + 0.50 M NaClO₄.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Temp. [°C]</th>
<th>[Cr(III)] [mM]</th>
<th>δ₁⁻¹⁸O/Cr</th>
<th>δ₂⁻¹⁸O/Cr</th>
<th>δ₁⁻¹⁸O/Cr</th>
<th>δ₂⁻¹⁸O/Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.1</td>
<td>1.41</td>
<td>0.61 ± 0.14</td>
<td>1.81 ± 0.13</td>
<td>2.43 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>24.9</td>
<td>1.04</td>
<td>0.80 ± 0.08</td>
<td>1.94 ± 0.08</td>
<td>2.73 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>24.9</td>
<td>0.86</td>
<td>0.72 ± 0.09</td>
<td>1.68 ± 0.09</td>
<td>2.40 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>24.9</td>
<td>1.29</td>
<td>0.73 ± 0.08</td>
<td>1.62 ± 0.08</td>
<td>2.35 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>5ᵃ</td>
<td>24.9₅</td>
<td>1.24</td>
<td>0.11 ± 0.05</td>
<td>0.13 ± 0.05</td>
<td>0.24 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>35.1</td>
<td>1.57</td>
<td>0.75 ± 0.07</td>
<td>1.60 ± 0.07</td>
<td>2.36 ± 0.03</td>
<td></td>
</tr>
</tbody>
</table>

k₁ (25°C): (7.6 ± 1.0) × 10⁻⁵ s⁻¹  k₂ (25°C): (1.23 ± 0.05) × 10⁻⁵ s⁻¹

ρ(k₁, k₂): 0.773

ᵃSee Experimental.

Table 2. Summary of kinetic data for water exchange in [Cr(NH₃)(OH₂)₂]⁺³ in 0.50 M HClO₄ + 0.50 M NaClO₄ at 25°C.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>[Cr(III)] [mM]</th>
<th>δ₁⁻¹⁸O/Cr</th>
<th>δ₂⁻¹⁸O/Cr</th>
<th>δ₁⁻¹⁸O/Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.08</td>
<td>0.77 ± 0.10</td>
<td>3.28 ± 0.10</td>
<td>4.04 ± 0.04</td>
</tr>
<tr>
<td>2</td>
<td>1.17</td>
<td>0.69 ± 0.11</td>
<td>3.45 ± 0.09</td>
<td>4.14 ± 0.05</td>
</tr>
<tr>
<td>3ᵃ</td>
<td>0.39</td>
<td>1.16 ± 0.17</td>
<td>1.78 ± 0.24</td>
<td>2.94 ± 0.12</td>
</tr>
<tr>
<td>4ᵃ</td>
<td>1.41</td>
<td>0.42 ± 0.05</td>
<td>0.27 ± 0.08</td>
<td>0.68 ± 0.03</td>
</tr>
</tbody>
</table>

k₁ (25°C): (2.8 ± 0.4) × 10⁻⁵ s⁻¹  k₂ (25°C): (0.449 ± 0.014) × 10⁻⁵ s⁻¹

ρ(k₁, k₂): 0.637

ᵃSee Experimental.
For both cations the larger rate constant has the smallest \( \delta' \)-value as preexponential factor, cf. Tables 1 and 2. This clearly identifies this rate constant as that associated mainly with the reactivity of the single water ligand trans to an ammonia ligand, in both complexes, cf. Fig. 1. The smaller constants consequently describe the reactivity of the two and four remaining water ligands, respectively, in the two complexes. In Ref. 3 the kinetic data for water exchange of the cis-diamminetetraaquachromium(III) ion has been analyzed in detail in terms of stereoretentive processes described by \( k_N \) and \( k_O \) and processes accompanied by water ligand isomerization, \( k_i \), cf. Fig. 2. Reactions of the present two complexes, in which also two types of water ligands are present in each, can be analyzed analogously, and from the exact expressions in the Appendix the following approximations are derived:

1. For \( \text{mer-}[\text{Cr(NH}_3)_3(\text{OH}_2)_3]^3+ \):

\[
\begin{align*}
  k_1 &\sim k_N + 4k_i \\
  k_2 &\sim k_O + 2k_i \\
  \delta' &\sim k_N - \frac{k_i(2k_N + k_O)}{k_1 - k_2}
\end{align*}
\]

Fig. 2. Water exchange in \( \text{mer-} \)triamminetriaqua- and amminepentaaquachromium(III) by stereoretentive processes, \( k_N \) and \( k_O \) paths, and by processes accompanied by isomerization, \( k_i \) paths.

and
\[
\delta_2 \sim \kappa_0 + \frac{k_4(2\kappa_N + \kappa_O)}{k_1 - k_2}
\]

Averaged data for the experiments 2–4 in Table 1 in combination with the assumption \(2\kappa_N \ll \kappa_O\), i.e. assuming that the purification steps mainly reduce the isotopic purity of the 'fast' water ligand site, allow the estimations of the following rate constants at 25 °C:
\[
k_1 \leq (0.16 \pm 0.07) \times 10^{-5} \text{ s}^{-1}
\]

\[
(7.0 \pm 1.0) \times 10^{-5} \text{ s}^{-1} \leq k_N \leq (7.6 \pm 1.0) \times 10^{-5} \text{ s}^{-1}
\]

and
\[
(0.91 \pm 0.15) \times 10^{-5} \text{ s}^{-1} \leq k_O \leq (1.23 \pm 0.05) \times 10^{-5} \text{ s}^{-1}
\]

Similarly for
2. \([\text{Cr(NH}_3\text{)}\text{OH}_2\text{]}_2]^{3+}\):
\[
k_1 \sim k_N + 8k_1
\]
\[
k_2 \sim k_O + 2k_1
\]
\[
\delta_1 \sim \kappa_N - \frac{k_4(4\kappa_N + \kappa_O)}{k_1 - k_2}
\]

and
\[
\delta_2 \sim \kappa_O + \frac{k_4(4\kappa_N + \kappa_O)}{k_1 - k_2}
\]

from which the averaged data for the experiments 1 and 2 in Table 2 and \(4\kappa_N \ll \kappa_O\) allow the estimations for the rate constants at 25 °C:
\[
k_1 \leq (0.03 \pm 0.02) \times 10^{-5} \text{ s}^{-1}
\]

\[
(2.5 \pm 0.4) \times 10^{-5} \text{ s}^{-1} \leq k_N \leq (2.8 \pm 0.4) \times 10^{-5} \text{ s}^{-1}
\]

and
\[
(0.39 \pm 0.04) \times 10^{-5} \text{ s}^{-1} \leq k_O \leq (0.449 \pm 0.014) \times 10^{-5} \text{ s}^{-1}
\]

For both cations the main reactivity is seen to be associated with the \(k_N\) and \(k_O\) paths. In view of the much smaller maximum value for the two \(k_1\) rate
constants it is, therefore, most likely that the present water exchange reactions are dominated by the stereoretention contributions to the $k_n$ and $k_0$ rate constants, a result which was also arrived at for the cis-diamminetetraaquachromium(III) ion.\textsuperscript{3}

With the present data in combination with the results in Refs. 2 and 3 the kinetics of water exchange of all ammineaquachromium(III) isomers have been investigated. A summary of these data classified according to the trans and cis ligands is given in Table 3. It is seen that the reactions are generally faster trans to an ammonia ligand than trans to a water ligand, and are decelerated by the introduction of cis water ligands although not in a regular fashion. This last point is illustrated more clearly in Table 4 where the difference between the observed reactivity of those reactants with from 1 to 3 cis water ligands, and that predicted by linear interpolation between the two reactants with 0 and 4 cis water ligands, i.e.

$$\delta[\Delta G^*(a_4, 1\text{aq})] = \Delta G^*(a_4, 4\text{aq}) - \frac{4-i}{4} \Delta G^*(a_4) - \frac{i}{4} \Delta G^*(a_{4\text{aq}})$$

have been calculated. All numbers in the table are seen to be negative corresponding to an increased reactivity, and are very similar for the two series of reactants, with the average values distributed roughly as 1.2:2:1 as demonstrated on Fig. 3. This result can be rationalized by considering the transition state geometry of Fig. 4, which has earlier been shown to rationalize data for some similar reactions.\textsuperscript{8} Fig. 5 demonstrates the possible transition state structures for the present reactions. If a similar geometry is assumed for all these transition states and the major cause of the cis effect is the ligand—ligand interactions between the four cis ligands and the entering and leaving water ligands, a linear variation of $\Delta G^*$ as function of the number of identical cis ligands will be expected. However, for the unsymmetrical transition state structures where the reacting water ligands are closest to two different cis ligands, i.e. the structures in Fig. 5 which have reacting water ligands marked with a double arrow, this geometry is not that with the minimum energy, and an energy lowered by an amount which will be called $\delta(\text{OH}_2)$ can be obtained by distorting this geometry, probably mainly by moving the reacting water ligand in a direction perpendicular to that mirror plane of symmetry of the idealized transition state, cf. Fig. 4, which contains the entering and leaving groups. This simple model predicts as a first approximation that the $\delta(\Delta G^*)$ values should be proportional to the number of reacting water ligands which are closest to two different cis ligands, i.e. should have the values $\delta(\text{OH}_2)$, $2\delta(\text{OH}_2)$, $2\delta(\text{OH}_2)$ and $\delta(\text{OH}_2)$. This

**Table 4.** 'Excess' cis effect for water exchange in [Cr(t)(a$_{4-1}$aq$_1$)OH$_2$]$^{3+}$ at 25 °C. Data from Table 3.

<table>
<thead>
<tr>
<th>${a_{4-1}\text{aq}_1}$</th>
<th>$t=\text{NH}_3$</th>
<th>$t=\text{OH}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta(\Delta G^*)$</td>
<td>$\delta(\Delta G^*)$</td>
</tr>
<tr>
<td></td>
<td>[KJ mol$^{-1}$]</td>
<td>[KJ mol$^{-1}$]</td>
</tr>
<tr>
<td>(NH$_3$)$_2$(OH$_2$)$_2$</td>
<td>$-0.51 \pm 0.10$</td>
<td>$-1.09 \pm 0.11$</td>
</tr>
<tr>
<td>cis-(NH$_3$)$_2$(OH$_2$)$_2$</td>
<td>$-0.91 \pm 0.17$</td>
<td>$-1.60 \pm 0.22$</td>
</tr>
<tr>
<td>trans-(NH$_3$)$_2$(OH$_2$)$_2$</td>
<td>$-1.59 \pm 0.35$</td>
<td>$-1.54 \pm 0.07$</td>
</tr>
<tr>
<td>(NH$_3$)(OH$_2$)$_3$</td>
<td>$-0.97 \pm 0.30$</td>
<td>$-0.53 \pm 0.12$</td>
</tr>
</tbody>
</table>

is seen to be in excellent agreement with the experiments shown in Fig. 3. From the data of this figure it can further be calculated that the lowering in ΔG* by distortions involving one of the reacting water ligands amounts to a value of δ(OH₂) about −0.73 kJ mol⁻¹.

This rationalization of the 'excess' reactivity of complexes with less than tetragonal symmetry may further be tested by analyzing the data for ammonia ligand aquation, which has also been systematically studied for the ammineaquachromium(III) isomers.¹ Table 5 gives data for the reactions trans to coordinated ammonia only, as the lack of a well-defined value for the rate constant for the pentaammineaquato trans-tetraamminediaqua-

<table>
<thead>
<tr>
<th>Reaction</th>
<th>δ(ΔG*) [kJ mol⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(NH₃)₅(OH₂)]</td>
<td>−1.05 ± 0.06</td>
</tr>
<tr>
<td>cis-(NH₃)₅(OH₂)₂</td>
<td>−1.06 ± 0.09</td>
</tr>
<tr>
<td>trans-(NH₃)₅(OH₂)₂</td>
<td>−0.81 ± 0.09</td>
</tr>
<tr>
<td>[(NH₃)₅(OH)₃]</td>
<td>−0.92 ± 0.09</td>
</tr>
</tbody>
</table>

This table, interpreted within this model, clearly show that distortions involving either the entering water molecule or the leaving ammonia ligand are energetically without consequence, i.e. either δ(OH₂) or δ(NH₃) is close to zero. The well-defined negative value for δ(OH₂) previously obtained makes the last possibility most likely, and gives the set of values δ(OH₂) ~ −0.92 kJ mol⁻¹ and δ(NH₃) ~ 0 kJ mol⁻¹. In good agreement with δ(OH₂) ~ −0.73 kJ mol⁻¹ obtained from the water exchange data.

The small value for δ(NH₃) may indicate significantly smaller ligand—ligand interactions when ammonia rather than water ligands are involved. This type of interaction is most likely greater also between the five nonreacting ligands in an associative transition state than in the ground state. The small δ(NH₃) value can, therefore, be taken as indirect evidence for the hypothesis that such interactions between the nonreacting ligands are also a contributing factor to the trans effect for the present series of reactions.

In conclusion, the present analysis of part of the kinetic cis effect strongly supports the hypothesis of an associative interchange mechanism, and the
structure shown in Fig. 4 has been demonstrated to be a good approximation to the idealized transition state geometry. This structure has earlier been arrived at through the analysis of the \( \Delta H^\circ_t \) vs. \( \Delta \chi \) variation as a function of a number of leaving X-ligands,⁸ and has now also been applied to the "excess" reactivity of complexes with less than tetragonal symmetry of the cis ligands, and is apparently able to explain this phenomenon for both of the two series of water exchange reactions and also for a series of much slower ammonia ligand aquation reactions.

Acknowledgement. The authors wish to thank the Geophysical Isotope Laboratory at the University of Copenhagen, particularly Dr. Niels Gundestrup, for carrying out the mass spectrometric analyses.

APPENDIX

The elementary reactions shown in Fig. 2 can be used to construct total reaction schemes for irreversible oxygen-18 aquation of labelled mer-triamminetriqua- and amminepentaaqua chromium-(III) as demonstrated in greater detail for the cis-diamminetetraaquachromium(III) ion in Ref. 3. In terms of experimentally determined quantities, cf. eqn. 1, it can be derived:

1. for mer-[Cr(NH₃)₃(OH₂)₃]³⁺:

\[
\delta_1' = \frac{(k_N + 9k_1 - k_2)(\chi_o(k_O + 2k_1 - k_I) - 4\chi_N k_I)}{(k_N + 8k_1 - k_2)(k_O + 2k_1 - k_I) - 4k_I^2}
\]

2. for [Cr(NH₃)(OH₂)₃]³⁺:

\[
\delta_2' = \frac{(k_N + 9k_1 - k_2)(\chi_o(k_O + 2k_1 - k_I) - 4\chi_N k_I)}{(k_N + 8k_1 - k_2)(k_O + 2k_1 - k_I) - 4k_I^2}
\]

In both cases \( \chi_N \) and \( \chi_O \) are the average number of oxygen-18 labelled water molecules trans to ammonia and water, respectively, at the start of the kinetic experiment.

REFERENCES


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