Reactions of Chloride Ions with Terminally Coordinated Water in Mono- and Dinuclear Chromium(III) Species. Acid Cleavage of Δ,Λ-μ-Hydroxo-bis[aquabis(ethylenediamine)chromium(III)] Species

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The cleavage of Δ,Λ-$(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)^{5+}$ in 12 M HCl at 1.0 °C has been studied by spectrophotometry and by analyzing the product solution by cation-exchange chromatography. The cleavage reaction gives primarily a mixture of cis-Cr $(en)_2(H_2O)_2^{3+}$, cis-$Cr(en)_2(H_2O)Cl^{2+}$ and cis-$Cr(en)_2Cl_2^{+}$. It is shown that the reaction involves three pathways: direct cleavage by aquation (k_3) or by anation (k_4), and cleavage via $\Delta,\Lambda,\Delta/\Delta$-$Cl(en)_2Cr(OH)Cr(en)_2(H_2O)^{4+}$. In the latter case, the rate-determining step is the reaction of Δ,Λ-$(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)^{5+}$ with Cl^- to give the dinuclear aquachloro species (k_5). The values of these pseudo first-order rate constants have been determined to be (12 M HCl, 1.0 °C): $k_3 = 1.2(2) \times 10^{-4}$ s^{-1}, $k_4 = 1.8(4) \times 10^{-4}$ s^{-1} and $k_5 = 5.1(4) \times 10^{-4}$ s^{-1}.

The cleavage reaction is followed by anation and aquation reactions of the mononuclear species. These reactions are only ca. 20 times slower than the cleavage reaction, and they therefore had to be included in the calculations of rate constants given above. A study of these reactions was therefore included. The activation parameters for the reactions of cis-$Cr(en)_2(H_2O)_2^{3+}$ and cis-$Cr(en)_2(H_2O)Cl^{2+}$ with chloride, and for the aquation of cis-$Cr(en)_2Cl_2^{+}$, have been determined. The aquation of cis-$Cr(en)_2(H_2O)Cl^{2+}$ is slow and only an upper-limit value for the rate constant has been obtained.

In a previous study[1] we showed that the cleavage of Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$ in 12 M HCl yields the mononuclear species cis-$Cr(en)_2Cl_2^{+}$, cis-$Cr(en)_2(H_2O)Cl^{2+}$ and cis-Cr $(en)_2(H_2O)_2^{3+}$. The reaction involves the intermediate and quantitative formation of the dinuclear species Δ,Λ/Λ,Δ-Cl $(en)_2Cr(OH)Cr(en)_2(H_2O)^{4+}$. The subsequent cleavage of this species was shown to involve direct cleavage by anation and by aquation, with $k_{an}/k_{aq} \approx 5$. It was shown that in addition to these direct cleavage reactions, cleavage via the species Δ,Λ-Cl$(en)_2Cr(OH)Cr(en)_2Cl^{3+}$ might also occur, and the contribution from this reaction path was estimated to lie in the range 0 to 13 %. The upper-limit value (13 %) corresponds to $k \approx 1.6 \times 10^{-3}$ s^{-1} for the reaction between chloride ions and Δ,Λ/Λ,Δ-Cl$(en)_2Cr(OH)Cr(en)_2(H_2O)^{4+}$ in 12 m HCl (1.0 °C), which is about 70 times larger than e.g. the rate constant for reaction between chloride ions and cis-$Cr(en)_2(H_2O)Cl^{2+}$ (see below).

A study of the cleavage of Δ,Λ-$(H_2O)(en)_2Cr(OH)Cr$ $(en)_2(H_2O)^{5+}$ in 12 M HCl was therefore initiated in the hope that with this system it would be possible to determine rate constants for the cleavage reactions as well as for the anation reaction. The cleavage reaction of Δ,Λ-$(H_2O)(en)_2$ $Cr(OH)(en)_2(H_2O)^{5+}$ is only about one order of magnitude faster than the subsequent anation and aquation reactions of the mononuclear species [see eqns. (1) and (2) below].

Knowledge of the thermodynamics and kinetics of these equilibria was therefore a prerequisite for a detailed study of the cleavage reaction. Some kinetic data for the anation and aquation reactions of the mononuclear species have been published previously, but they do not allow extrapolation to the conditions relevant to this work.[2–5] A study of these reactions was therefore included in the present work.

Experimental

Materials and instruments. The compounds cis-$[Cr(en)_2$ $(H_2O)_2]Br_3 \cdot 2H_2O$,[6] cis-$[Cr(en)_2]Cl_2H_2O$,[7] Δ,Λ-$[(HO)(en)_2$ $Cr(OH)Cr(en)_2(OH)](ClO_4)_3 \cdot 2H_2O$,[8] and Δ,Λ-$[Cl(en)_2Cr$ $(OH)Cr(en)_2Cl](ClO_4)_2Cl \cdot 2H_2O$[1] were prepared as described in the literature. All other chemicals were of analytical grade. Absorption spectra were recorded on a Perkin-Elmer Lambda Diode Array spectrophotometer.

Kinetic data. Pseudo first-order rate constants, k_{obs}, were calculated from the absorbance A as a function of time by means of non-linear regression analysis, using the expression $A = A_\infty + (A_0 - A_\infty)\exp(k_{obs} \times t)$.
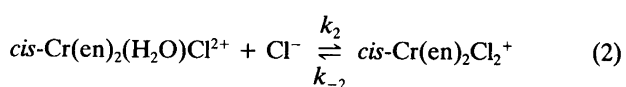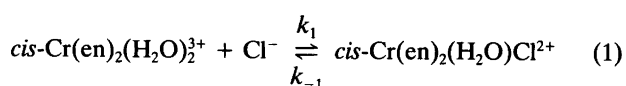
The calculations of the rate constant for the cleavage reaction were made using absorbances measured at 4 different wavelengths in the region 498–503 nm.

The rate constants for the equilibration between cis-Cr (en)$_2$Cl$_2^+$ and cis-Cr(en)$_2$(H$_2$O)Cl^{2+} in 12 M HCl were calculated using absorbances at 251 different wavelengths in the region 350–600 nm. The calculations of the rate constants for equilibration between cis-Cr(en)$_2$(H$_2$O)Cl^{2+} and cis-Cr (en)$_2$(H$_2$O)$_2^{3+}$ were made using absorbances measured at the three wavelengths 383, 449 and 513 nm. The activation parameters for the reactions of the mononuclear species have been calculated from measurements at 1.0 and 25.0 °C, using the expression $k_r = (k_B T/h)\exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT)$.

Cation-exchange chromatography. The components of product solutions for the cleavage reaction, and of the equilibrium solutions of the mononuclear species (in 12 M HCl), were separated using a column of Dowex 50W-X2 cation exchanger and analyzed for chromium(III) and coordinated chloride, as described previously.[1] All determinations were made in duplicate.

Results

Anation and aquation of the mononuclear species in 12 M HCl. The equilibria between the mononuclear species in 12 M HCl [eqns. (1)–(2)] were studied at 0.0, 25.0 and 40.0 °C. At each temperature, solutions of cis-[Cr(en)$_2$Cl$_2$]Cl·H$_2$O or cis-[Cr(en)$_2$(H$_2$O)$_2$]Br$_3$·2H$_2$O in 12 M HCl were kept until equilibrium had been attained (8×$t_{\frac{1}{2}}$, see below) and were then analysed using cation-exchange chromatography. Identical values were obtained for solutions initially containing either cis-Cr(en)$_2$Cl$_2^+$ or cis-Cr(en)$_2$(H$_2$O)$_2^{3+}$. Only cis-Cr(en)$_2$Cl$_2^+$ and cis-Cr(en)$_2$(H$_2$O)Cl^{2+} could be detected in the equilibrium solutions and the recovery was 99 %. This gave the thermodynamic parameters reported in Table 1.

$$\text{cis-Cr(en)}_2\text{(H}_2\text{O)}_2^{3+} + \text{Cl}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{cis-Cr(en)}_2\text{(H}_2\text{O)Cl}^{2+} \quad (1)$$

$$\text{cis-Cr(en)}_2\text{(H}_2\text{O)Cl}^{2+} + \text{Cl}^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{cis-Cr(en)}_2\text{Cl}_2^+ \quad (2)$$

The rate constants k_2 and k_{-2} were determined by following the change in absorbance of solutions of Δ,Λ-[Cl(en)$_2$Cr(OH)Cr(en)$_2$Cl](ClO$_4$)$_2$Cl·H$_2$O in 12 M HCl. As described previously,[1] a solution of this dinuclear species in 12 M HCl yields very rapidly ($t_{\frac{1}{2}} < 1$ s at 25 °C) a mixture of cis-Cr(en)$_2$(H$_2$O)Cl^{2+} and cis-Cr(en)$_2$Cl$_2^+$. The equilibration reaction between these species was then studied spectrophotometrically in the wavelength region 350–600 nm. Well-defined isosbestic points at (ε/M^{-1} cm^{-1}, λ/nm) = (57,383), (25,449) and (72,513) were observed for the entire reaction, which gave constant final spectra. The change of absorbance with time followed first-order kinetics, and from the expressions $k_{obs} = k_2[\text{Cl}^-] + k_{-2}$ and $K_2 = k_2/k_{-2}$ the rate constants were then calculated (Table 1).

The reaction of cis-[Cr(en)$_2$(H$_2$O)$_2$]Br$_3$·2H$_2$O in 12 M HCl was monitored at the wavelengths 383, 449 and 513 nm. At these wavelengths, the molar absorbances of cis-Cr (en)$_2$(H$_2$O)Cl^{2+} and cis-Cr(en)$_2$Cl$_2^+$ are identical, and the change of absorbance is therefore due only to the equilibration reaction between cis-Cr(en)$_2$(H$_2$O)$_2^{3+}$ and cis-Cr (en)$_2$(H$_2$O)Cl^{2+} [eqn. (1)]. The change of absorbance with time followed first-order kinetics and gave well-defined values of k_{obs}. Since $K_1 > 2$ M^{-1} it follows that $k_1[\text{Cl}^-] >> k_1$ for 12 M HCl, and therefore $k_{obs} = k_1[\text{Cl}^-] + k_{-1} \approx k_1[\text{Cl}^-]$. This gave the values for k_1 listed in Table 1. It is noted that the present values are in reasonable agreement with those published previously, considering the fact that different ionic strengths have been used (see footnote to Table 1). Combination of the previously determined value $k_{-1} = 2.8 \times 10^{-5}$ s^{-1} (0.1 M HNO$_3$)^2 and the value $k_1 = 8.4 \times 10^{-5}$ M^{-1} s^{-1} (12 M HCl) determined in this work gives the following rough estimate for K_1 at 25 °C: $K_1 = k_1/k_{-1} \approx 3$ M^{-1}. This value agrees with the estimated lower-limit value $K_1 > 2$ M^{-1} for 12 M HCl obtained in this study.

Cleavage of Δ,Λ-(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$(H$_2$O)$^{5+}$ in 12 M HCl. The cleavage of Δ,Λ-(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$ (H$_2$O)$^{5+}$ in 12 M HCl yields the mononuclear species cis-Cr (en)$_2$Cl$_2^+$, cis-Cr(en)$_2$(H$_2$O)Cl^{2+} and cis-Cr(en)$_2$(H$_2$O)$_2^{3+}$. The reaction was studied by spectrophometry and by analysis of the product solution by cation-exchange chromatography.

Table 1. Thermodynamic and kinetic data[a] for the equilibria [eqns. (1) and (2)] between the mononuclear species in 12 M HCl at 25 °C.

Constant	ΔH^0 or $\Delta H^{\ddagger}$/kJ mol^{-1}	ΔS^0 or $\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
$K_1 > 2$ M^{-1}	–	–
$k_1 = 8.4(1) \times 10^{-5}$ s^{-1} M^{-1}	85(1)	–37(5)
$k_{-1} < 4 \times 10^{-5}$ s^{-1}	–	–
$K_2 = 0.21(1)$ M^{-1}	–2(3)	–21(10)
$k_2 = 4.3(4) \times 10^{-5}$ s^{-1} M^{-1}	87(5)	–36(15)
$k_{-2} = 2.0(1) \times 10^{-4}$ s^{-1}	89(4)	–16(14)

[a]The following selected[5] values have been reported: $k_{-1} = 2.8 \times 10^{-5}$ s^{-1} (25 °C, 0.1 M HNO$_3$);[2] $k_{-2} = 3.3 \times 10^{-4}$ s^{-1}, $\Delta H^{\ddagger} = 86$ kJ mol^{-1} and $\Delta S^{\ddagger} = -24$ J mol^{-1} K^{-1} (25 °C, 0.1 M HNO$_3$),[2,3] $k_2 = 1.3 \times 10^{-4}$ s^{-1} M^{-1} (35 °C, 11 M HCl)[4] to be compared with the value $k_2 = 1.5 \times 10^{-4}$ s^{-1} M^{-1} (35 °C, 12 M HCl) calculated from activation parameters given above.

Scheme 1. Formal reaction scheme for the cleavage in 12 M HCl (Cl^-, H^+ and H_2O have been omitted).

The pseudo first-order rate constant, k_{obs}, for the cleavage reaction was determined from the spectrophotometric measurements. The influence of the subsequent reactions of the mononuclear products (see above) had to be taken into account. The reactions of these species are about 20 times slower than the cleavage reaction, and their influence was eliminated by restricting the calculations to absorbances measured in a wavelength region, viz. 498–503 nm, for which the cleavage reaction gives rise to a large change in absorbance and the subsequent reactions produce an almost negligible change in absorbance. This procedure gave the same k_{obs} values for calculations based upon measurements for $2t_1$ and $7t_1$, respectively. In this way an average value of $k_{obs} = 8.1(1) \times 10^{-4}$ s^{-1} was obtained on the basis of 3 experiments.

Analysis of the product solution by cation-exchange chromatography showed the presence of all three mononuclear species, and the cleavage reaction may therefore be described formally as shown in Scheme 1, in which the rate constants k_a, k_b and k_c are composite terms. The product distribution, measured after a given reaction time, will depend not only on the ratio between these constants, but will also be influenced by the anation and aquation reactions of the mononuclear species (with rate constants k_1, k_2 and k_{-2}; k_{-1} can be ignored, as discussed above). In the Appendix it is shown how k_a, k_b and k_c can be calculated

when the rate constants k_{obs}, k_1, k_2 and k_{-2} and the product distribution at a given time are known. For a reaction time of 120 min, the following product distribution[1] was found: 40.6(15) % cis-Cr(en)$_2$(H$_2$O)$_2^{3+}$, 32.6(8) % cis-Cr(en)$_2$(H$_2$O)Cl^{2+}, 26.5(7) % cis-Cr(en)$_2$Cl$_2^+$, and less than 1 % of the dinuclear species. This gave the values $k_a = 4.33$ (13)$\times10^{-4}$ s^{-1}, $k_b = 1.82(16) \times 10^{-4}$ s^{-1}, and $k_c = 1.95$ (14)$\times10^{-4}$ s^{-1}.

The "rate constants" k_a, k_b and k_c are composite terms which may yield true rate constants as follows: As shown in Scheme 2, the cleavage of Δ,Λ-(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$ (H$_2$O)$^{5+}$ may proceed by aquation or by anation; this does not, however, explain the formation of significant amounts of cis-Cr(en)$_2$Cl$_2^+$. The formation of this species shows that in addition to the direct cleavage reactions (k_3 and k_4), cleavage via the intermediate $\Delta,\Lambda/\Lambda,\Delta$-(H$_2$O)(en)$_2$Cr(OH) Cr(en)$_2$Cl^{4+} also plays a significant role. The cleavage of this species has been studied recently[1] and has been shown to afford the mononuclear species in yields of 43.4 % (diaqua), 18.5 % (aquachloro) and 38.1 % (dichloro). The observed pseudo first-order rate constant for the cleavage of this species is $k_6 = 0.012$ s^{-1} in 12 M HCl (1.0 °C). This is

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[1] The recovery of chromium(III) was 97 %. The yields of the mononuclear species have been corrected so that their sum equals the "theoretical" yield (99.7 %) calculated from $k_{obs} = 8.1 \times 10^{-4}$ s^{-1}.

Scheme 2. Cleavage in 12 M HCl at 1.0 °C (Cl^-, H^+ and H_2O have been omitted). The pseudo first-order constants k_3, k_4 and k_5 have been determined in this work. The constant k_6, which is the *observed* rate constant for the cleavage of $\Delta,\Lambda/\Lambda,\Delta$-(H$_2$O)(en)$_2$Cr(OH)Cr (en)$_2$Cl^{4+}, and the product distribution for this reaction have been taken from Ref. 1.

Table 2. Pseudo first-order rate constants for cleavage by aquation (k_{aq}) and anation (k_{an}) in 12 M HCl at 1.0 °C.[a]

Dinuclear species	k_{aq}/s^{-1}	k_{an}/s^{-1}	% Anation
$\Delta,\Lambda\text{-}(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)^{5+}$	$1.2(2)\times10^{-4}$	$1.8(4)\times10^{-4}$	59
$\Delta,\Lambda/\Lambda,\Delta\text{-}(H_2O)(en)_2Cr(OH)Cr(en)_2Cl^{4+}$	$2(1)\times10^{-3}$	$9(1)\times10^{-3}$	$82^{b,c}$
$\Delta,\Lambda\text{-}Cl(en)_2Cr(OH)Cr(en)_2Cl^{3+}$	$> 10^{-2}$	$> 4\times10^{-2}$	$80^{b,d}$

[a] k_{aq} and k_{an} are in each case defined as exemplified in Scheme 2 for $k_{aq} = k_3$ and $k_{an} = k_4$. [b] From Ref. 1. [c] Cleavage by anation may occur in two different ways (Ref. 1). [d] For 9 M HCl, the values $k_{aq} = 6(1)\times10^{-3}$ s^{-1}1 and $k_{an} = 1.7(2)\times10^{-2}$ s^{-1} at 1.0 °C have been reported.[1]

about 15 times larger than the k_{obs} value for the cleavage of $\Delta,\Lambda\text{-}(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)^{5+}$. The rate-determining step for the cleavage via the aquachloro species must therefore be the anation reaction k_5 (Scheme 2). This leads to eqns. (3)–(5), in which $x = 0.434(10)$, $y = 0.185$ (10) and $z = 0.381(10)$ are the yields (mole fractions) of the mononuclear species formed by cleavage of $(H_2O)(en)_2$ $Cr(OH)Cr(en)_2Cl^{4+}$.

$$k_a = k_3 + \tfrac{1}{2} k_4 + k_5 x \tag{3}$$

$$k_b = \tfrac{1}{2} k_4 + k_5 y \tag{4}$$

$$k_c = k_5 z \tag{5}$$

This gave the values $k_3 = 1.2(2)\times10^{-4}$ s^{-1}, $k_4 = 1.8(4)\times10^{-4}$ s^{-1} and $k_5 = 5.1(4)\times10^{-4}$ s^{-1} (12 M, 1.0 °C).

Discussion

In Tables 2 and 3, the rate constants for the cleavage and the anation reactions, respectively, studied in the present work are compared with those for the related dinuclear species $\Delta,\Lambda\text{-}Cl(en)_2Cr(OH)Cr(en)_2Cl^{3+}$ and $\Delta,\Lambda/\Lambda,\Delta\text{-}$ $Cl(en)_2Cr(OH)Cr(en)_2(OH_2)^{4+}$.

All three dinuclear species are cleaved by anation and aquation pathways, and the contribution from the anation path is in the region 60–80 % (Table 2). In contrast, as shown recently, the first bridge cleavage of $\Delta,\Lambda\text{-}(en)_2Cr$ $(OH)_2Cr(en)_2^{4+}$ proceeds, under the same conditions, almost 100 % by an anation path.[1] The cleavage reactions of the dinuclear dichloro and aquachloro species are believed to proceed by a dominant acid-catalyzed pathway.[1] Likewise, we assume that the cleavage of $\Delta,\Lambda\text{-}(H_2O)(en)_2Cr$

$(OH)Cr(en)_2(H_2O)^{5+}$ in 12 M HCl is also acid-catalyzed. The acid-catalyzed cleavage of hydroxo-bridged species is generally assumed to involve protonation of the hydroxo bridge, and there is indirect evidence that the aqua-bridged intermediates are very labile and that they are strong acids with $K_a \gg 1$.[9] Because of these extreme properties it has never been possible to obtain spectroscopic evidence for the existence of these species. In the present study we find that the ligand-field spectrum of $\Delta,\Lambda\text{-}[(HO)(en)_2Cr(OH)$ $Cr(en)_2(OH)](ClO_4)_3\cdot2H_2O$ in 12 M HCl (at $t = 0$) is very similar to that reported[8] for the diaqua species in 1 M HClO$_4$ [$(\varepsilon/M^{-1}$ cm^{-1}, $\lambda/nm)_{max} = (164,504)$; $(100,380)$ and $(161,503)$; $(100,378)$, respectively]. The great similarity of the spectra indicates that there is no substantial protonation of the hydroxo bridge even in 12 M HCl.

The rate of the cleavage reactions is seen (Table 2) to increase in the order diaqua < aquachloro < dichloro (decreasing charge) for both the aquation and the anation cleavage paths. The acid strength of the aqua-bridged intermediates is expected, on the basis of charge considerations, to decrease in the same order, and the trend is therefore reasonable in terms of an acid-catalyzed mechanism.

The rate constant for the reaction of chloride with the dinuclear diaqua species lies in the region of that recently reported for the corresponding reaction of chloride with the dinuclear aquachloro species (Table 3). This is a satisfactory result, since chloride would be expected a priori to react with the two species at comparable rates, cf. the very similar rate constants for the corresponding reactions of the mononuclear species, as discussed below.

The dinuclear diaqua species reacts about ten times faster with chloride than does the mononuclear species. It would seem tempting to explain this difference on the basis of the greater charge of the dinuclear species. However, we

Table 3. Pseudo first-order rate constants for the anation reactions of mono- and dinuclear species in 12 M HCl at 1.0 °C.

Reactant	Product	k/s^{-1}
$cis\text{-}Cr(en)_2(H_2O)_2^{3+}$	$cis\text{-}Cr(en)_2(H_2O)Cl^{2+}$	$4.6(2)\times10^{-5}$ [a,b]
$cis\text{-}Cr(en)_2(H_2O)Cl^{2+}$	$cis\text{-}Cr(en)_2Cl_2^{+}$	$2.2(6)\times10^{-5}$ [a,c]
$\delta,\Lambda\text{-}(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)^{5+}$	$\Delta,\Lambda/\Lambda,\Delta\text{-}(H_2O)(en)_2Cr(OH)Cr(en)_2Cl^{4+}$	$5.1(4)\times10^{-4}$ [d]
$\Delta,\Lambda/\Lambda,\Delta\text{-}(H_2O)(en)_2Cr(OH)Cr(en)_2Cl^{4+}$	$\Delta,\Lambda\text{-}Cl(en)_2Cr(OH)Cr(en)_2Cl^{3+}$	$< 2\times10^{-3}$ [e]

[a] Calculated from the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values given in Table 1. [b] $k_1\times12$ s^{-1}. [c] $k = k_2\times12$ s^{-1}. [d] $k = k_5$ (Scheme 2). [e] From Ref. 1.

$$k_a = \frac{(A/2D_0)(k_1' - k_{obs})}{(e^{-k_{obs}t} - e^{-k_1't})} \tag{12}$$

$$k_b = \frac{(k_{-2} + k_2' - k_{obs})}{(e^{-(k_2' + k_{-2})t} - e^{k_{obs}t})} \times \left\{ \frac{k_{-2}(1 - e^{-(k_2' + k_{-2})t})}{k_2' + k_{-2}} - \frac{B}{2D_0} + \frac{k_a(k_1' - k_{-2})(e^{-(k_2' + k_{-2})t} - e^{-k_1't})}{(k_1' - k_{obs})(k_{-2} + k_2' - k_1')} \right\}$$

$$- \frac{k_a(k_1' - k_{-2})}{k_1' - k_{obs}} + k_{-2} \tag{13}$$

note firstly that the rate constants for the reactions of the two mononuclear species, rather surprisingly, do not reflect any influence of the charge of the reacting species: $k/k_2 \cong 2$ at 25 °C, which is equal to the statistically expected ratio, and the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are equal, within experimental error, for the two reactions (Table 1). Secondly, when comparing the reactions of the mono- and dinuclear species, in this context it is probably not the charge per species but the charge per chromium(III) which should be considered. The latter ratio is within the same range for the mononuclear (2–3) and the dinuclear (2–2.5) species. Charge effects are therefore not likely to explain the observed differences. Alternatively, we propose tentatively that the enhanced reactivity of the dinuclear species is caused essentially by a labilizing effect of the hydroxo bridge upon the cis ligands. This suggestion is in keeping with the general observation that the reactions of binuclear hydroxo-bridged chromium(III) species with neutral or anionic ligands are much faster than those of the "parent" mononuclear species.[9]

Appendix

Calculation of the rate constants k_a, k_b and k_c in Scheme 1. The concentrations at time t are denoted:

$A = [cis\text{-}Cr(en)_2(H_2O)_2^{3+}]$

$B = [cis\text{-}Cr(en)_2(H_2O)Cl^{2+}]$

$C = [cis\text{-}Cr(en)_2Cl_2^{+}]$

$D = [(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)^{5+}]$

At $t = 0$, $D = D_0$ and $A = B = C = 0$. This gives eqn. (6).

$$D_0 = D + A/2 + B/2 + C/2. \tag{6}$$

The observed rate constant for the cleavage reaction is expressed in eqn. (7):

$$k_{obs} = k_a + k_b + k_c \tag{7}$$

in which k_a, k_b and k_c are the pseudo first-order rate constants defined as shown in Scheme 1. Since $K_1 \times [Cl^-] > 24$

for $[Cl^-] = 12$ M (Table 1), it is assumed that k_{-1} can be ignored. The differential equations according to Scheme 1 are shown in eqns. (8)–(11), in which $k_1' = k_1[Cl^-]$ and $k_2' = k_2[Cl^-]$.

$$dA/dt = 2k_aD - k_1'A \tag{8}$$

$$dB/dt = 2k_bD + k_1'A - k_2'B + k_{-2}C \tag{9}$$

$$dC/dt = 2k_cD + k_2'B - k_{-2}C \tag{10}$$

$$dD/dt = -k_{obs}D \tag{11}$$

Integration and some rearrangement yield eqns. (12)–(13).

The rate constants k_1', k_2', k_{-2} and k_{obs} (12 M HCl, 1.0 °C) are all known: $k_{obs} = 8.1(2) \times 10^{-4}$ s^{-1}, and from the activation parameters in Table 1 it is calculated that $k_1' = k_1 \times 12 = 4.6(2) \times 10^{-5}$ s^{-1} and $k_2' = k_2 \times 12 = 2.2(6) \times 10^{-5}$ s^{-1} and $k_{-2} = 0.79(15) \times 10^{-5}$ s^{-1}. $A/2D_0$ and $B/2D_0$ at $t = 7200$ s are also known: $A/2D_0 = 0.406$ and $B/2D_0 = 0.326$. The constants k_a, k_b and k_c may then be calculated from eqns. (12), (13) and (7).

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