Base hydrolysis of macrocyclic chromium(III) complexes. Importance of ion-pair formation for kinetics and mechanism †

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A series of *cis* and *trans* complexes of the general formula $[Cr(cyc)(OH_2)X]^{2+}$, where cyc is the macrocyclic tetraamines *meso-* or *rac-* 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and $X^- = NCS^-$, N_3^- and Cl^-, have been prepared in solution *via* anation of the diaqua complexes. The kinetics of the monodendate X ligand release in alkaline media have been studied at a range of temperatures and hydroxide concentrations at ionic strengths of 1.0 or 2.0 M using $NaClO_4$, NaBr or NaCl as "inert" electrolytes. A higher order than linear dependence of the pseudo-first-order rate constant on the hydroxide concentration has been observed for all the systems investigated. These results have been rationalized in terms of specific ion-pair interactions between the macrocyclic chromium(III) reactants and counterions of the supporting electrolytes, followed by proton transfer in the hydroxide ion pair to give a reactive conjugate base.

Introduction

Base hydrolysis of robust metal complexes was first investigated more than half a century ago. The first investigations were concentrated on amine complexes of cobalt(III), and a large portion of later investigations have also been directed towards complexes of this metal ion.[1–3] The stoichiometry of almost all the processes investigated involve replacement of a halide or pseudo-halide ligand with a hydroxide ligand, and the reactions are frequently accompanied by stereochemical changes. The rate expression shows that this reaction type is second-order: first-order in complex and first-order in hydroxide, corresponding to a mechanism that involves deprotonation of an amine ligand.

Metal centres other than cobalt(III) have been significantly less thoroughly studied, partly due to preparative difficulties, and partly due to more complicated stoichiometric reaction schemes. Some important features of chromium(III) reactions in alkaline media, such as lower rate and higher stereochemical rigidity in comparison to analogous Co(III) species, sol–gel equilibria and thermodynamic trends to transformation into chromium(VI) are discussed in the literature.[1,4–9]

For amine complexes of chromium(III) with simple amine ligands, this frequently involves reactions leading to amine ligand aquation in competition with halide or pseudo-halide aquation, usually followed by rapid precipitation of chromium(III) hydroxide. Chromium(III) complexes of macrocyclic amine ligands are much more robust and, in particular, complexes of the 14-membered tetraamine cyclam-type ring system may be treated with base at elevated temperatures for extended periods of time without aquation of the macrocyclic ligand and hydroxide precipitation.[10] For chromium(III) complexes of the unsubstituted cyclam ligand, slow *cis* to *trans* isomerization

takes place, but in the two hexamethyl substituted cyclam-type ligands *meso-* and *rac-*5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, cyc*a* and cyc*b*, isomerization has not yet been observed for chromium(III), contrasting with the behaviour of the analogous rhodium(III) complexes, where an effective *cis* to *trans* isomerization of the cyc*b* complex occurs, in particular under preparative conditions.[11]

The hexamethylcyclam ligands, cyc*a* and cyc*b*, collectively referred to as cyc, stereospecifically form chromium(III) complexes of the types *trans*-$[Cr(cyca)XY]^{z+}$ and *cis*-$[Cr(cycb)$-$XY]^{z+}$, and the robustness and stereochemical rigidity of these Cr(cyc) units in combination with two coordination positions significantly more labile than the coordinated amine ligand has allowed the isolation of complexes with a great variety of X,Y ligand combinations.[12] The present work deals predominantly with base hydrolysis of complexes of the general formula $[Cr(cyc)(OH)X]^+$, with $X^- = NCS^-$, N_3^- and Cl^-. These complexes were selected because they enable a comparison of the reactivity of the *cis* and *trans* isomers, including an evaluation of the labilizing effect of a hydroxide ligand at *cis* and *trans* positions to the substituted ligand and an evaluation of the kinetic consequences of amine ligand deprotonation. The base hydrolysis reactions have been studied using three types of supporting electrolytes at two different ionic strengths in order to evaluate the role of second sphere interactions.

Experimental

Materials

cis-$[Cr(cycb)(H_2O)_2]Br_3 \cdot 2H_2O$ and *cis*-$[Cr(cycb)$-$(H_2O)Cl](ClO_4)_2 \cdot 3H_2O \cdot 0.4HClO_4$ were prepared by literature methods.[12] *trans*-$[Cr(cyca)(H_2O)_2]Br_3 \cdot 3H_2O$ and *trans*-$[Cr(cyca)Cl_2]Cl$ were prepared by methods similar to those described for analogous cyc*b* complexes.[12] Other chemicals were the best available commercial grades.

CAUTION: the perchlorate salt described here is potentially explosive and should be handled accordingly.

Analysis

Chromium contents were determined using a Varian ABQ-20 ASA spectrometer.

Preparations

All the solutions used in preparations were made using doubly distilled water and purged with N_2 or Ar to avoid contamination with CO_2. Sephadex SP–C-25 (Na^+) was used for chromatographic separations. The concentration of the eluted complexes was usually about 5×10^{-3} M.

1 *cis*-[Cr(cyc*b*)(H$_2$O)(NCS)]$^{2+}$ solutions. 33 mg of *cis*-[Cr(cyc*b*)(H$_2$O)$_2$]Br$_3$·2H$_2$O was dissolved in 10 cm^3 of water. 12.2 mg NaNCS (a 3-fold molar excess) was added. The resulting solution was left in the dark in a closed bottle overnight and then applied to a 12 × 2 cm Sephadex SP–C-25 column. A pink component was clearly separated from *cis*-[Cr(cyc*b*)(NCS)$_2$]$^+$ by elution with 0.5 M NaBr + 0.01 M HBr. Characteristic spectral data for *cis*-[Cr(cyc*b*)(H$_2$O)(NCS)]$^{2+}$: λ_{max}/nm (ε_{max}/ M^{-1} cm^{-1}) 525 (175), 387 (92), 312 (4330).

2 *cis*-[Cr(cyc*b*)(H$_2$O)(N$_3$)]$^{2+}$ solutions. 325 mg of *cis*-[Cr(cyc*b*)(H$_2$O)$_2$]Br$_3$·2H$_2$O was dissolved in 48 cm^3 of water and acidified with 2 cm^3 1 M HBr. 32.5 mg NaN$_3$ (a 10-fold molar excess) was added gradually, while the pH of the solution was kept at 4 by addition of 1 M HBr. The resulting solution was left in the dark in a closed bottle overnight and then applied to a 10 × 2 cm Sephadex SP–C-25 column. A pink–violet component was clearly separated from *cis*-[Cr(cyc*b*)(N$_3$)$_2$]$^+$ and *cis*-[Cr(cyc*b*)(H$_2$O)$_2$]$^{3+}$ by elution with 0.5 M NaBr + 0.001 M HBr. The solution was kept in a cool, dark place. Characteristic spectral data for *cis*-[Cr(cyc*b*)(H$_2$O)(N$_3$)]$^{2+}$: λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 544 (193), 407 (121), 277 (4300), 231 (9590).

3 *cis*-[Cr(cyc*b*)(H$_2$O)Cl]$^{2+}$ solutions. About 1.5 mg of *cis*-[Cr(cyc*b*)(H$_2$O)Cl](ClO$_4$)$_2$ was dissolved in 3.5 cm^3 of 1 M Na(Br$^-$, Cl$^-$, ClO$_4^-$) and 0.1 M H(Br$^-$, Cl$^-$, ClO$_4^-$) to avoid fast base hydrolysis, and was immediately used for kinetic measurements, being converted to the hydroxo form at the beginning of the measured reactions with the requisite excess of NaOH. Characteristic spectral data for *cis*-[Cr(cyc*b*)(H$_2$O)-Cl]$^{2+}$: λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 554 (192), 406 (135).

4 *trans*-[Cr(cyc*a*)(H$_2$O)(NCS)]$^{2+}$ solutions. 33 mg of *trans*-[Cr(cyc*a*)(H$_2$O)$_2$]Br$_3$·3H$_2$O was dissolved in 100 cm^3 of water and 12 mg of NaNCS (a 3-fold molar excess) was added. The resulting solution was left in the dark in a closed bottle overnight, and then applied to a 9 × 2 cm Sephadex SP–C-25 column. A peach-coloured component was clearly separated from *trans*-[Cr(cyc*a*)(H$_2$O)$_2$]$^{3+}$ by elution with 0.5 M NaBr + 0.01 M HBr. Characteristic spectral data for *trans*-[Cr(cyc*a*)-(H$_2$O)(NCS)]$^{2+}$: λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 503 (38), 425 (29), 311 (3510).

5 *trans*-[Cr(cyc*a*)(H$_2$O)(N$_3$)]$^{2+}$ solutions. 334 mg of *trans*-[Cr(cyc*a*)(H$_2$O)$_2$]Br$_3$·3H$_2$O was dissolved in 48 cm^3 of water and acidified with 2 cm^3 1 M HBr. 32.5 mg NaN$_3$ (a 10-fold molar excess) was added gradually, while the pH of the solution was kept at 4 by addition of 1 M HBr. The resulting solution was left in the dark in a closed bottle overnight, and then applied to a 10 × 2 cm Sephadex SP–C-25 column. A yellow–orange component was clearly separated from *trans*-[Cr(cyc*a*)(N$_3$)$_2$]$^+$ and *trans*-[Cr(cyc*a*)(H$_2$O)$_2$]$^{3+}$ by elution with 0.5 M NaBr + 0.001 M HBr. The solution was kept in a cool, dark place. Characteristic spectral data for *trans*-[Cr(cyc*a*)(H$_2$O)(N$_3$)]$^{2+}$: λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 524 (108), 380 (85), 270 (3560), 237 (6740).

6 *trans*-[Cr(cyc*a*)(H$_2$O)Cl]$^{2+}$ solutions. About 0.2 g of *trans*-[Cr(cyc*a*)Cl$_2$]Cl was dissolved in 20 cm^3 of water and heated at 100 °C for 25 min. The resulting solution was cooled to room temperature and applied to a 8 × 2 cm Sephadex SP–C-25 column. A dark-red component was clearly separated from *trans*-[Cr(cyc*a*)Cl$_2$]$^+$ and *trans*-[Cr(cyc*a*)(H$_2$O)$_2$]$^{3+}$ by elution with 0.5 M Na(Br$^-$, Cl$^-$, ClO$_4^-$) + 0.01 M H(Br$^-$, Cl$^-$, ClO$_4^-$). Note: elution of the green *trans*-[Cr(cyc*a*)Cl$_2$]$^+$ with 0.1 to 0.3 M NaCl has first to be performed to avoid its precipitation as bromide or perchlorate salts on the column. After removal of the *trans*-[Cr(cyc*a*)Cl$_2$]$^+$ component, the eluent may be changed to bromide or perchlorate. Characteristic spectral data for *trans*-[Cr(cyc*a*)(H$_2$O)Cl]$^{2+}$: λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 530 (19), 372 (63), 428 (34).

Attempts to detect conjugate bases

The hydroxo complexes are potential Brønsted acids and the amine nitrogens and the hydroxide ligand can, in principle, be deprotonated. This was tested spectroscopically by recording UV-Vis spectra of 1 mM chromium(III) in solutions with hydroxide within the concentration range 0.1 to 1.9 M at $I = 2.0$ M. Within the experimental accuracy, the spectra were the same for all examined solutions at $t = 0$.

The possibility of amine nitrogen deprotonation during base hydrolysis was demonstrated by the observation of exchange of nitrogen-bound hydrogens in alkaline media. The IR spectra, obtained with a Spectrum 2000 Perkin Elmer FT-IR spectrometer, demonstrate that the N–H/N–D stretching vibration after deuteration is shifted from 3209 to 2269 and from 3240 to 2291 cm^{-1} for the *cis* and *trans* isomers, respectively. The exchange studies were carried out using 99.97% D_2O from Dr Glaser AG, Basel, Switzerland.

Kinetic measurements

The reactions were followed spectrophotometrically using an RC-Partner computer-controlled Perkin-Elmer Lambda-17 spectrophotometer equipped with a Perkin-Elmer digital temperature controller, a Hewlett Packard 8453 diode-array spectrophotometer equipped with a Peltier HP 89090A digital temperature controller and a Shimadzu UV-1601 PC spectrophotometer equipped with a Shimadzu CPS-240A digital temperature controller. Subsecond rate measurements were made with an Applied Photophysics stopped-flow spectrometer.

Absorbance–time data were collected at single wavelengths, usually in the range 237–295 nm, with the exception of the measurements carried out using the diode-array instrument. Data up to 3–4 half-lives were used for the rate constants calculations. The kinetic experiments covered the temperature range 10–75 °C and the concentration ranges: 0.5–3 mM [Cr^{III}] and 0.02–0.8 M [OH$^-$] for $I = 1.0$ M and 0.05–1.9 M [OH$^-$] for $I = 2.0$ M. Half lives, $t_{1/2}$, of the experiments varied between 20 ms and 11500 s. Reactions carried out in multisecond time scales were initiated by injection of 0.05 cm^3 of a solution of the chromium(III) complex to 2 cm^3 of a thermostatted solution containing all the other components. The reactions performed with the stopped-flow instrument were initiated by mixing two thermostated solutions, one containing the chromium(III) complex prepared as described above and the other containing different amounts of NaOH. The ionic strength was kept at the desired level, 1 or 2 M, with Na(Br$^-$, Cl$^-$, ClO$_4^-$) in both solutions.

Most of the kinetic runs were repeated at least three times. Pseudo-first-order rate constants, k, were calculated by non-linear regression analysis using the function: $A_{obs}(t) \approx A_{calc}(t) = A_0 + A_1 \cdot e^{-kt}$. The relative error for a single rate constant was ≤ 1% and reproducibility of the runs was characterized by relative standard deviations ≤ 2%, usually ≈ 1%.
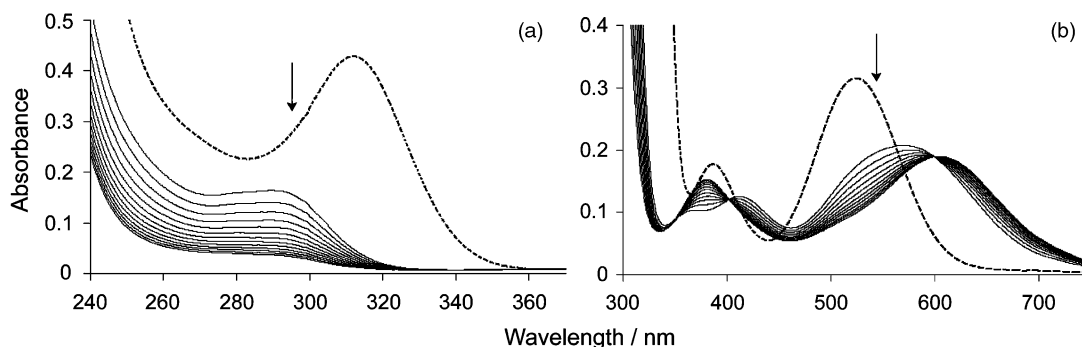
Fig. 1 (a) Changes in UV spectrum during base hydrolysis of the *cis*-[Cr(cyc*b*)(OH)(NCS)]$^+$, [Cr^{III}] = 1 × 10^{-4} M, [OH$^-$] = 0.1 M, I = 1.0 M NaClO$_4$, T = 30 °C, scans every 8 min; (---) *cis*-[Cr(cyc*b*)(H$_2$O)(NCS)]$^{2+}$. (b) Changes in Vis spectrum during base hydrolysis of the *cis*-[Cr(cyc*b*)(OH)(NCS)]$^+$, [Cr^{III}] = 2 × 10^{-3} M, [OH$^-$] = 0.1 M, I = 1.0 M NaClO$_4$, T = 30 °C, scans every 8 min; (---) *cis*-[Cr(cyc*b*)(H$_2$O)(NCS)]$^{2+}$.

Results

Anation of [Cr(cyc)(H$_2$O)$_2$]$^{3+}$ by X$^-$, X$^-$ = Cl$^-$, N$_3^-$ or NCS$^-$, in weakly acidic aqueous solution gives mixtures which allow the isolation of [Cr(cyc)(H$_2$O)X]$^{2+}$ complexes by ion exchange chromatography or precipitation of suitable salts. The water ligand in these species is deprotonated in basic solution, as evidenced by the spectral changes, and the resulting hydroxo complex undergo slow substitution of the X ligand to give [Cr(cyc)(OH)$_2$]$^+$. The spectral changes within the whole UV-Vis range are consistent with a simple process in which the monodentate ligand is released without competitive or concurrent reactions; an example for the *cis*-NCS isomer is shown in the Fig. 1. This simple reaction course is substantiated by chromatographic analysis of acidified reaction mixtures at various conversion degrees during the reaction.

Single wavelength kinetic data obey a pseudo-first-order rate law at a sufficiently large excess of hydroxide over chromium(III), and pseudo-first-order rate constants, k_{obs}, have been determined as a function of temperature, of hydroxide concentration, and at different constant ionic strengths maintained by chloride, bromide or perchlorate, *cf.* the Experimental section. The pseudo-first-order rate constants, k_{obs}, are collected in the ESI.

The X ligand release processes are dominated by a markedly increased reactivity in basic solutions as compared to the reactivity in acidic solutions. In a weakly basic solution, this stems from the well-established accelerating effect of a hydroxide ligand as compared to a water ligand. In stronger basic solution, a further increase in reactivity is seen, which must be ascribed to a further deprotonation of the chromium(III) reactant. This effect is seen both for *trans*-[Cr(cyc*a*)Cl$_2$]$^+$ and for the [Cr(cyc)(OH)X]$^+$ complexes. Consequently, the effect must arise from deprotonation of the amine ligand, an effect which especially for cobalt(III) complexes is very well established.[1]

The non-linear dependence of the k_{obs} as a function of the hydroxide concentration, which is particularly apparent at high hydroxide concentrations, *cf.* Fig. 2, could be ascribed to a multiple deprotonation of the coordinated macrocyclic amine ligand.

This assumption would lead to a positive curvature of the k_{obs} *vs.* [OH$^-$] dependence. However, the reproduction of the k_{obs} values using a mathematical model based upon double deprotonation of the chromium(III) reactant is significantly inferior to the reproduction obtained by using a model operating with a competitive ion-pair formation between chromium(III) reactant and the two anions of the aqueous medium, followed by a single deprotonation of the amine nitrogen. A simple stoichiometric reaction scheme for such a model is given in Scheme 1, where k_Y and k_{OH} are the first-order rate constants and K_Y is the equilibrium constant for competitive outer-sphere complex formation between Y$^-$ and OH$^-$. The conjugate base formed *via* proton transfer in the M·OH ion pair is not explicitly shown in this scheme.

Scheme 1
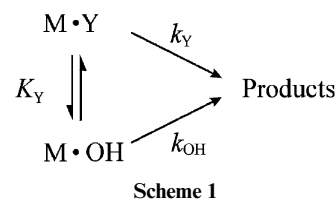
Experiments conducted under pseudo-first-order conditions give rise to the expression for k_{obs} shown in eqn. 1:

$$k_{obs} = \frac{k_Y c_Y + k_{OH} K_Y c_{OH}}{c_Y + K_Y c_{OH}} \tag{1}$$

where $c_Y + c_{OH} = I$, I being the ionic strength. The model presented here operates with 3 independent parameters for each reactant, in each ionic medium. Such parameter sets for a single reactant at a single ionic strength, however, would all have to describe the same reactivity in the ionic medium limit of a pure aqueous hydroxide solution. It should consequently be noted that the k_{OH} parameter will only be dependent upon the ionic strength of the aqueous medium, in contrast to the k_Y and K_Y parameters, which also depend upon the identity of the supporting Y anion. Table 1 gives the reactivity parameters k_Y and k_{OH}, and the pre-equilibrium constant, K_Y, at 25 °C, and also the temperature dependence of these parameters.

Discussion

The X ligand reactivity pattern, as measured both by the k_{OH} and the k_Y rate constants, is the same for all the systems investigated: NCS$^-$ is more robustly bound than N$_3^-$, which is significantly more strongly bound than Cl$^-$. This reactivity order is that normally seen for these ligands coordinated to chromium(III).[13,14] Some quantitative differences are apparent, however, as demonstrated by the relative k_{OH} and k_Y rate constants; k_Y values given for the chloride medium:

		NCS$^-$ <	N$_3^-$ <<	Cl$^-$
k_{OH}	*cis*:	1	2.9	4.7×10^4
k_{OH}	*trans*:	1	8.2	3.9×10^2
k_{Cl}	*cis*:	1	2.4	3.5×10^4
k_{Cl}	*trans*:	1	4.7	5.1×10^2

Variations are similar for the k_{OH} and k_{Cl} constants, but a significantly greater span of values is seen for the *cis* complexes than for the *trans* complexes. The very similar relative rates for the k_{OH} and k_{Cl} paths are somewhat surprising, since the k_{OH} path is expected to be a composite reaction involving a proton

Table 1 Rate constants, k_{OH} and k_Y (Y = Cl, Br or ClO$_4$), and ion-pair formation constants, K_Y, at 25 °C, activation energies, E_a, and reaction enthalpies, $\Delta_r H°$, cf. Scheme 1 and eqn. 1. Standard deviations are given in parentheses

Reactant	I/M E_a/kJ mol^{-1}	k_{OH}/s^{-1} E_a/kJ mol^{-1}	k_{Cl}/s^{-1} E_a/kJ mol^{-1}	K_{Cl} $\Delta H°$/kJ mol^{-1}	k_{Br}/s^{-1} E_a/kJ mol^{-1}	K_{Br} $\Delta H°$/kJ mol^{-1}	k_{ClO_4}/s^{-1} E_a/kJ mol^{-1}	$K_{ClO_4}\Delta H°$/ kJ mol^{-1}
cis-[Cr(cycb)(OH)Cl]$^+$	1	4.5(3) × 10^1 51(3)	5.90(2) 86.9(2)	0.18(2) 54(3)	5.37(2) 88.4(2)	0.16(2) 52(3)	4.02(2) 86.3(3)	0.27(2) 50(3)
cis-[Cr(cycb)(OH)(N$_3$)]$^+$	1	2.80(1) × 10^{-3} 109(2)	4.05(7) × 10^{-4} 110.5(9)	0.27(2) 11(4)	3.34(6) × 10^{-4} 110.7	0.22(2) 11(4)	3.30(8) × 10^{-4} 99.5(14)	0.37(3) 11(4)
	2	5.1(2) × 10^{-3} 111(2)	— —	— —	— —	— —	2.57(10) × 10^{-4} 109(2)	0.33(3) −6(4)
cis-[Cr(cycb)(OH)(NCS)]$^+$	1	9.5(6) × 10^{-4} 117(3)	1.71(4) × 10^{-4} 115.9(14)	0.29(4) 5(6)	1.52(4) × 10^{-4} 115.1(14)	0.28(3) 3(6)	1.34(4) × 10^{-4} 112.6(18)	0.47(6) 0(6)
	2	1.74(4) × 10^{-3} 123.0(12)	— —	— —	— —	— —	1.46(2) × 10^{-4} 115.1(9)	0.33(3) −2(2)
trans-[Cr(cyca)(OH)Cl]$^+$	1	6.1(2) × 10^{-1} 75(3)	8.1(2) × 10^{-3} 90(2)	0.53(3) 22(2)	7.6(2) × 10^{-3} 92(2)	0.47(2) 24(3)	5.7(2) × 10^{-3} 90(2)	0.42(2) 21(3)
trans-[Cr(cyca)(OH)(N$_3$)]$^+$	1	1.28(1) × 10^{-2} 116.0(16)	7.5(8) × 10^{-5} 103(12)	0.56(2) 6(3)	5.6(7) × 10^{-5} 94(14)	0.47(1) 7(3)	4.7(6) × 10^{-5} 121(13)	0.42(3) 5(2)
	2	2.88(5) × 10^{-2} 118.1(19)	— —	— —	— —	— —	4.5(4) × 10^{-5} 106(9)	0.22(1) 4(3)
trans-[Cr(cyca)(OH)(NCS)]$^+$	1	1.57(3) × 10^{-3} 137(2)	1.6(2) × 10^{-5} 142(13)	0.54(2) 2(3)	2(1) × 10^{-6} 205(14)	0.53(3) −8(3)	9(2) × 10^{-6} 145(20)	0.48(2) −2(3)
	2	3.39(7) × 10^{-3} 137(2)	— —	— —	— —	— —	1.3(3) × 10^{-5} 105(20)	0.30(1) −8(3)
trans-[Cr(cyca)Cl$_2$]$^+$	1	2.78(7) × 10^2 102(2)	— —	0.270(7) −17(2)	— —	0.221(6) −16(2)	— —	— —

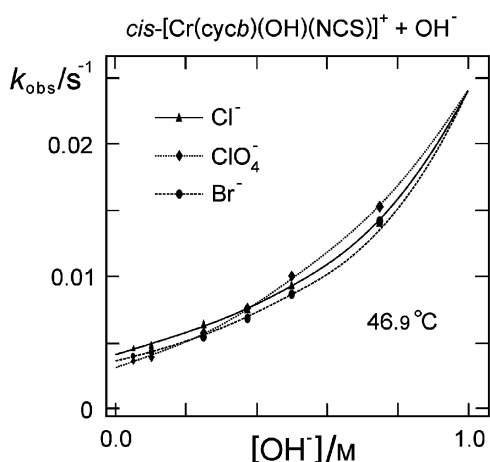**Fig. 2** Dependence of the observed rate constant on OH$^-$ ion concentration for different electrolytes, I = 0.1 M.

transfer reaction in the ion pair followed by a substitution reaction in the generated conjugate base, whereas the k_{Cl} path is expected to describe a simple substitution reaction in the hydroxo complex. The observed similarity in the relative rates could perhaps point towards the importance of an intramolecular proton transfer in the hydroxy complex, giving a much more reactive conjugate base deprotonated at an amine nitrogen atom. This speculation, however, must await further work. The similar variations of the k_{OH} and k_{Cl} rate constants are further supported by surprisingly constant k_{OH}/k_{Cl} ratios for the individual complexes, the values for cis complexes being around 7 and values for the trans complexes significantly higher, at around 10^2. Contrary to this apparent order, k_{cis}/k_{trans} ratios vary in a more irregular way, as demonstrated by the values:

		N$_3^-$ <	NCS$^-$ <<	Cl$^-$
k_{OH}	k_{cis}/k_{trans}:	0.22	0.61	74
k_{Cl}	k_{cis}/k_{trans}:	5.4	11	7.3 × 10^2

The variations in the reaction rates all correlate well with the differences in activation energies. Increases in activation energies for the k_{OH} path are, however, for the most part compensated for by more favourable activation probabilities. As an example of this, it may be noted that the k_{OH} ratio of 4.7 × 10^4 for aquation of Cl$^-$ vs. NCS$^-$ in the cis complex corresponds to a free energy difference of about 27 kJ mol^{-1}, whereas the activation energy difference between the two processes is about 66 kJ mol^{-1}, cf. Table 1. A comparison of the similar trans complexes shows a rate constant ratio of 3.9 × 10^2, corresponding to a free energy difference of about 15 kJ mol^{-1}. Again, the activation energy difference of about 62 kJ mol^{-1} is significantly larger. Variations in rate constants for the k_Y path, however, are almost exclusively functions of activation energy differences. Comparing again aquation of Cl$^-$ vs. NCS$^-$ in the cis complex, a rate ratio of 3.5 × 10^2, corresponding to a free energy difference of 26 kJ mol^{-1}, is found, a value comparable to the activation energy difference of about 29 kJ mol^{-1} (cf. Table 1). The activation energies for the k_Y path for the trans complexes are not sufficiently well defined to allow meaningful comparisons.

The variation in ionic strength from 1 to 2 M doubles the value of k_{OH} for all the complexes studied, which is in agreement with the supposition of proton transfer from the chromium(III) complex to hydroxide in the ion pair as a prerequisite for the reaction to take place. In contrast to the marked variation of the k_{OH} rate constant as function of the ionic strength, the k_Y rate constants are almost constant, although rather large standard deviations on most of the rate constants make detailed comparisons difficult. The constancy, however, other ionic medium effects being neglected, is not in disagreement with the supposed intimate reaction mechanism.

Minor variations of the k_Y rate constant are seen as a function of the "inert" anion of the solvent medium. The variation is the same for all the reactants, and shows a decrease in the reaction rate on going from Cl$^-$ to Br$^-$ to ClO$_4^-$. A further discussion of this decrease of the value of the rate constant is difficult in the absence of detailed structural information on second sphere interactions, which at present is not available for the reactants. The K_Y ion-pair constant is an attempt at a statistical description of the ionic second sphere interactions, and some general tendencies in the data are apparent, but partly contradictory in terms of attempts of formulating a simple theoretical foundation. For cis complexes, larger K_Y values are seen along the series Br$^-$ to Cl$^-$ to ClO$_4^-$, whereas for trans complexes, the value of K_Y decreases along the series Cl$^-$ to Br$^-$ to ClO$_4^-$. Both series of complexes shows decreasing K_Y values with an increase in the ionic strength, although the variation is

not quantitatively the same for the different reactants. Again the absence of information on second sphere interactions makes a detailed interpretation of these results difficult.

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