Chromium(III) Complexes of Macrocyclic Ligands. Kinetics and Equilibria of the Reaction between cis-Diaqua(rac-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)chromium(III) and Chloride

L. MØNSTED [a] and O. MØNSTED [b]

[a] Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark and [b] Department of Inorganic Chemistry, H.C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

The reaction between the title chromium(III) complex: cis-$[Cr(cycb)(OH_2)_2]^{3+}$ and chloride has been investigated in 1.00 M $(Na,H)(ClO_4,Cl)$ at 25–40 °C.

Rates and activation parameters for aquation of chloride bound to chromium(III) are within the range normally found for such reactions, but unusually large acidity constants of the aqua-chromium(III) species make reactivity contributions by deprotonated species dominating even in 1 M acid. The equilibrium constant for formation of the 1:1 inner sphere complex, 4.4 ± 0.3 M^{-1} in 1.00 M $HClO_4$ at 25 °C, is larger than usual for chloridochromium(III) complexes and has a smaller temperature dependence. These observations are rationalized in relation to data for other chloridochromium(III) systems in terms of the solvational properties of the cations.

Many chromium(III) complexes of macrocyclic ligands are extraordinarily stable towards aquation of this ligand type in both acid and basic solution, which allows substitution reactions at unblocked coordination positions to be studied under very varied conditions.

Selected macrocyclic ligands can give complexes with high degrees of stereoselectivity in substitution or ligand modification processes, and complexes of the cycb-tetraamine shown in Fig. 1 are a good example of such behaviour. Thus the Cr(cycb)-moiety coordinates only
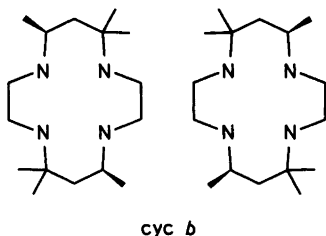

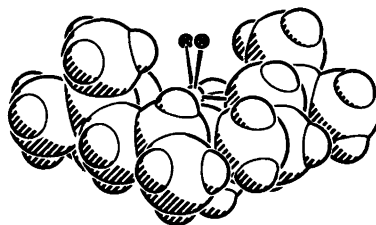*Fig. 1.* rac-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane.

Fig. 2. Structure of the Cr(cycb) moiety, *cf.* Ref. 2. The two x-marked circles show unoccupied ligand positions ≈ 2.0 Å away from the chromium atom.
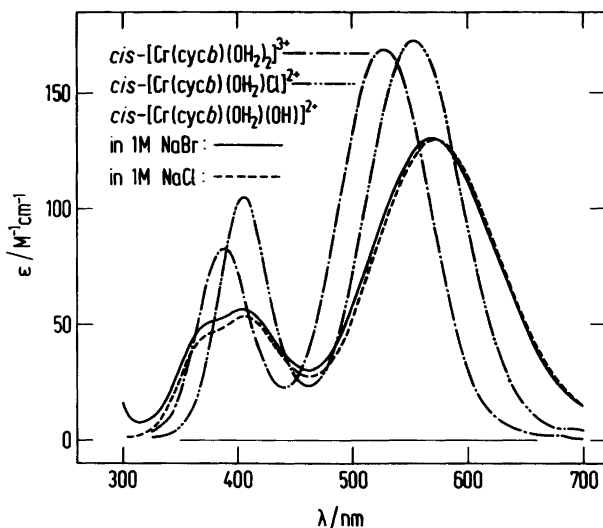
Fig. 3. Visible absorption spectra of *cis*-[Cr(cyc*b*)(OH₂)₂]³⁺, *cis*-[Cr(cyc*b*)(OH₂)-Cl]²⁺ and ~*cis*-[Cr(cyc*b*)(OH₂)(OH)]²⁺. The shift towards red of the spectrum of the aquahydroxo species in chloride as compared to bromide solution is in agreement with a significant content of the chloridohydroxo species.

linear or planar ligator systems,[1] and the optical isomers are capable of a very effective chiral discrimination. Both these observations can be rationalized by considering the detailed *cis*-complex geometry as shown in Fig. 2.

The kinetics of such processes are of considerable interest also from an applicational point of view, but possibilities for detailed investigations are frequently limited by the solubilities of reactant or reaction product salts in solutions of common poorly coordinating anions. The present investigation was mainly undertaken to assess the applicability of chloride containing aqueous solutions for investigations of reactions of cyc*b*-chromium(III) complexes.

RESULTS AND DISCUSSION

cis-Diaqua-cyc*b*-chromium(III) reacts with chloride to give aquachlorido- and dichlor-idotetraaminechromium(III) of which the latter cation precipitates as the insoluble chloride salt.[1] At lower chloride concentrations, solutions prepared from the diaqua- or aquachlorido complex remain homogeneous, however, and have, eventually, identical absorption spectra. The spectral changes during the equilibration process show isosbestic points at the wavelengths expected for a mixture of only the diaqua- and aquachlorido species, *cf.* Fig. 3. Spectra of equilibrated solutions depend on the chloride concentration and can be used to determine the innersphere equilibrium constant for formation of the 1:1 complex, K_X(obs). These data are shown in Fig. 4 A.

The time dependence of the spectral changes observed during the equilibration process is in agreement with simple first order kinetics, but as shown in Fig. 4 B the first order rate constants, k(obs), depend in a complicated manner on both the hydrogen ion and chloride concentrations.
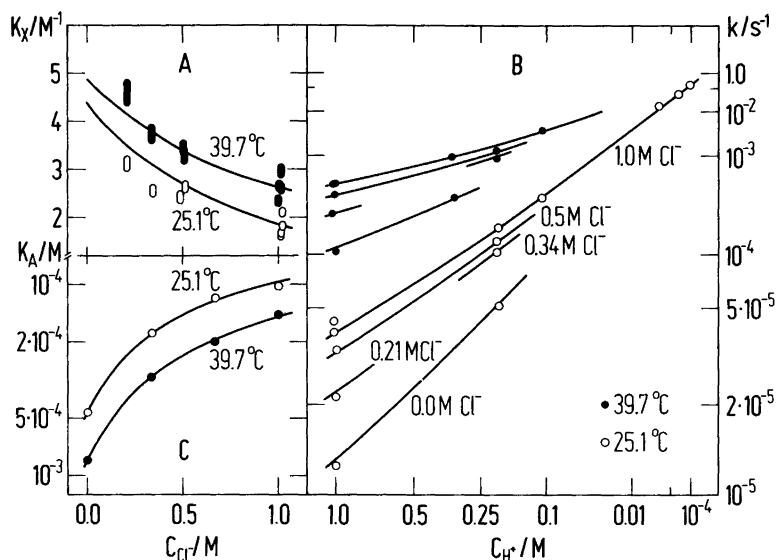
Fig. 4. A: inner sphere equilibrium constant, K_X, B: first order equilibration rate constant, k, and C: first acid dissociation constant, K_A, as function of [Cl⁻] and [H⁺]. In all three figures the solid curves are calculated from the determined parameters. The trend of rate constants with the chloride concentration in Fig. 4 B is the same at both temperatures.

The rate of equilibration is slow in strong acid and has a half life of about 15 hours in 1 M perchloric acid at 25 °C. At lower acidities it is much faster, however, and at hydrogen ion concentrations below the millimolar level equilibration is complete within seconds. The complexes can therefore be titrated in chloride containing solutions without complications

Table 1. Acid dissociation constants for some amineaquachromium(III) complexes in 1.00 M Na(ClO₄,X) at 25 °C and 40 °C. X=Cl, Br.

Complex	Temp/ °C	[Cl⁻]/M	[Br⁻]/M	-log(K_1/M)	-log(K_2/M)
cis-[Cr(cyc*b*)(OH₂)₂]³⁺	25	–	–	3.331±0.012	7.019±0.014
		0.33	–	3.742±0.012	7.089±0.015
		0.67	–	3.929±0.011	7.105±0.015
		1.00	–	3.986±0.013	7.151±0.015
		–	0.33	3.414±0.012	7.066±0.015
		–	0.67	3.464±0.012	7.089±0.015
		–	1.00	3.486±0.012	7.112±0.015
	40	–	–	3.08±0.03	6.69±0.03
		0.33	–	3.52±0.02	6.75±0.03
		0.67	–	3.70±0.03	6.76±0.04
		1.00	–	3.84±0.02	6.73±0.03
cis-[Cr(cyclam)(OH₂)₂]³⁺	25	–	–	4.212±0.012	7.25±0.03
		1.00	–	4.324±0.011	7.31±0.02
[Cr(NH₃)₅(OH₂)]³⁺		–	–	5.180±0.011	
		0.50	–	5.267±0.012	
		1.00	–	5.315±0.012	
		–	0.50	5.225±0.010	
		–	1.00	5.261±0.012	

from time dependent electrode potentials, and acid dissociation constants, K_A(obs), for the system at a series of chloride concentrations are shown in Fig. 4 C.

The K_A(obs) values are seen to depend strongly upon the chloride concentration. As shown in Table 1 the effect of bromide is much smaller as is also that of halogenide on the acid dissociation constants of both pentaammineaqua- and the 'macrocyclic' *cis*-diaqua(1,4,8,11-tetraazacyclotetradecane)chromium(III), *cis*-[Cr(cyclam)(OH$_2$)$_2$]$^{3+}$, cations. This comparison suggests that the major part of the large effect of chloride on the K_A(obs) values in Fig. 4 C originates in specific chemical effects and that unspecific electrostatic effects accompanying the change of the anion of the ionic medium from perchlorate to chloride is less important in this context.

The fact that the K_X(obs)-values are a function of the chloride concentration is clear evidence, however, for the breakdown of the constant ionic medium concept for the present changes of electrolyte. Recently this was also shown in detail for the much simpler system:[3]

$$[Cr(NH_3)_5(OH_2)]^{3+} + Br^- \rightleftharpoons [Cr(NH_3)_5Br]^{2+}$$
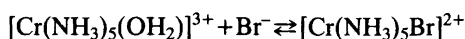
Here the difference between the kinetically determined equilibrium constant:

$$K_{kin} \approx \frac{d\ k(obs)/d\ [Br^-]}{k(obs)} \quad \text{for } [Br^-] \to 0.0\ M$$

and that obtained as the concentration quotient, K_X(obs), was interpreted in terms of a parameter, α_{aq}, characteristic for the effect of replacing bromide for perchlorate, on the aquation rate constant of the pentaamminebromidochromium(III) ion:

$$K_{kin} \approx K_X(obs) + \alpha_{aq} \tag{1}$$

At the molecular level α_{aq} originates from preferential ion pair formation between the higher charged cations and bromide rather than perchlorate, and a simple reaction scheme incorporating this type of ionic interactions and also the observed hydrogen ion concentration dependence is shown in Fig. 5. Within this reaction scheme the present experimental data are represented by:

$$K_X(obs) \approx K_X(calc) = K_X \frac{1 + K_{I,X}[X]}{1 + K_I[X]} \tag{2}$$

$$K_A(obs) \approx K_A(calc) = \frac{K_A + K'_A K_X[X] + K_A K_{I,B}[X]}{1 + (K_I + K_X)[X] + K_X K_{I,X}[X]^2} \tag{3}$$

and

$$k(obs) \approx k(calc) = \frac{k_- + k_{-X} K_{I,X}[X] + k_{-B} K'_A/[H^+]}{1 + K_{I,X}[X] + K'_A/[H^+]}$$

$$+ \frac{k_- K_X + k_{-X} K_X K_{I,X}[X] + k_{-B} K_X K'_A/[H^+]}{1 + K_I[X] + K_A/[H^+] + K_A K_{I,B}[X]/[H^+]} [X] \tag{4}$$

The experiments are well described by this model as shown by the good agreement between observed and calculated quantities in Figs. 4 A–C. Parameters for the ionic interactions between the dipositive cations and chloride are not well defined, however, and
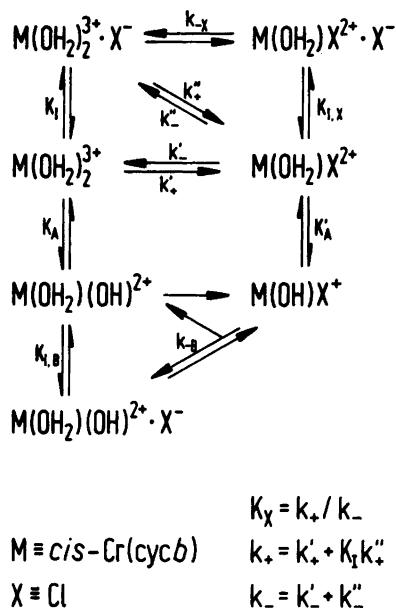
$$M(OH_2)_2^{3+} \cdot X^- \xrightleftharpoons[\ ]{k_{-x}} M(OH_2)X^{2+} \cdot X^-$$

Fig. 5. Reaction scheme for equilibration of
cis-Cr(cyc*b*) in chloride containing solution.

$$M \equiv cis\text{-}Cr(cyc b)$$
$$X \equiv Cl$$

$$K_X = k_+ / k_-$$
$$k_+ = k'_+ + K_I k''_+$$
$$k_- = k'_- + k''_-$$

the reaction scheme may be simplified by setting $K_{I,B}$ and $K_{I,X}$ equal to 0.0 M without affecting the agreement in Figs. 4 A–C. Parameter values evaluated within this reduced reaction scheme are given in Table 2.

In this context it is of interest to note that the α_{aq} parameter for the pentaamminechromium(III) system, with parameters from Fig. 5, is given by:

$$\alpha_{aq} \approx K_{I,X} \left(\frac{k_{-X}}{k_-} - 1 \right)$$

Experimentally it has the value: $\alpha_{aq} \approx 0.28 \pm 0.05$ M^{-1}, which makes the $K_{I,X}$ parameter important for this system. It should be realized, however, that the present much more complicated cyc*b*-chromium(III) system may well have an α parameter of the same order of magnitude without this being well defined from the experiments.

Table 2. Kinetic and thermodynamic parameters for the equilibration of *cis*-cyc*b*-chromium(III) in 1.00 M (Na,H)(ClO$_4$,Cl), *cf.* the reaction scheme in Fig. 5.[a]

| Parameter | Parameter value | | ΔH^b [kJ mol^{-1}] | ΔS^b [J mol^{-1} K^{-1}] |
	25.1 °C	39.7 °C		
K_X/M^{-1}	4.4±0.3	4.9±0.3	6±5	+32±17
K_I/M^{-1}	1.26±0.17	0.85±0.12		
-log(K_A/M)	3.331±0.006	3.079±0.012	30.8±1.7	+40±6
-log(K'_A/M)	4.40±0.11	4.5±0.2		
k_-/s^{-1}	(3.0±0.6)·10^{-6}	(3.1±0.3)·10^{-5}	122±12	+50±40
$k_{-B}K'_A$/M s^{-1}	(10.0±0.4)·10^{-6}	(8.0±0.2)·10^{-5}	108±3	+13±10

[a] $K_{I,X}=K_{I,B}=0.0$ M^{-1}. [b] ΔH°, ΔH^* or $\Delta H^*+\Delta H^\circ$ and analogously for ΔS depending upon the parameter.

Table 3. Comparison of data for complex formation between chromium(III) and chloride at 25.0 °C in 1.00 M $(Na,H)ClO_4$, *cf.* the reaction scheme in Fig. 5.

Reaction product	k_-/s^{-1}	$\Delta H^*/kJ\ mol^{-1}$	K_X/M^{-1}	$\Delta H°/kJ\ mol^{-1}$	$-\log(K_A/M)$	Ref.
cis-[Cr(cycb)(OH₂)Cl]²⁺	$(3.0\pm0.6)\cdot10^{-6}$	122±12	4.4±0.3	6±5	3.331±0.006	This work
cis-[Cr(NH₃)₄(OH₂)Cl]²⁺	$5.4\cdot10^{-6}$	89.1±2.0			4.961±0.015	4,5
[Cr(NH₃)₅Cl]²⁺	$9.8\cdot10^{-6}$	90.4±1.3	0.2		5.180±0.011	6,7,8,3, This work
[Cr(OH₂)₅Cl]²⁺	$0.277\cdot10^{-6}$	101.7±0.8	0.10	25±3	4.29	9,10,11
cis-[Cr(cycb)(OH)Cl]⁺	0.25±0.06		0.38±0.10		7.019±0.014	This work
cis-[Cr(NH₃)₄(OH)Cl]⁺	0.22				7.53±0.03	12,5

Table 3 compares the present kinetic and thermodynamic data with a selected set of literature data. The two most prominent features are seen to be the significant acidity of the aqua-cyc*b*-chromium(III) complexes, and the significant magnitude of the formation constant for *cis*-[Cr(cyc*b*)(OH$_2$)Cl]$^{2+}$. The magnitude of these parameters makes reactivity contributions from deprotonated species dominating in even very strong acid solution and also makes *cis*-[Cr(cyc*b*)(OH)Cl]$^+$ more stable than most other tetraaminechloridohydroxo-chromium(III) species, *cf.* also the absorption spectra in Fig. 3.

These differences are most readily interpreted in terms of differences in the solvation of the cations. Solvation of complexes of the macrocyclic ligands may be expected to be less dependent upon the total charge of the complex than solvation of complexes with simpler ligands. Hence the 'macrocyclic' complexes will be stronger acids and form stronger complexes with anions than complexes with a larger charge dependence of the solvational stabilization. The effect of solvation has been clearly demonstrated by a study of the complex formation between hexaaquachromium(III) and chloride at a series of water activities in perchloric acid:[10] Increasing stability of the monochlorido complex is accompanied by decreasing enthalpy and constant entropy of formation as the water activity decreases in accord with the present rationalization of data for the 'macrocyclic' complexes.

EXPERIMENTAL

Chemicals. *Cis*-[Cr(cyc*b*)(OH$_2$)$_2$]Br$_3 \cdot 2\frac{1}{2}$H$_2$O, *cis*-[Cr(cyc*b*)(OH)$_2$]ClO$_4 \cdot 2$H$_2$O and *cis*-[Cr(cyc*b*)(OH$_2$)Cl](ClO$_4$)$_2 \cdot x$ H$_2$O $\cdot y$ HClO$_4$ were prepared by literature methods.[1] Other chemicals were the best available commercial grades which were purified as necessary.

Kinetic measurements. The equilibration reactions were followed spectrophotometrically using thermostatted cells in either a Cary 118 C or a Zeiss DMR spectrophotometer. Slow reactions were followed at 330–720 nm, and faster reactions at a single wavelength usually between 550 and 630 nm. 3-chloropyridine buffer solutions were used to maintain a constant hydrogen ion-concentration at the lower range of acidities. The 3-chloropyridinium ion has $-\log(K_1/M) \approx 3.18\pm0.04$ in 1.00 M NaCl and 3.37 ± 0.03 in 1.00 M NaClO$_4$ at 25 °C.

Potentiometric measurements were performed as previously described.[5]

Methods of analysis. Hydrogen ion and chloride concentrations were determined by standard titrimetric procedures involving OH$^-$ and Ag$^+$. Chromium was determined by atomic absorption spectrometry because the macrocyclic amine complexes are only very slowly oxidized to chromate(VI) in base.

Methods of calculation. All parameter values were determined by minimizations within the framework of nonlinear regression analysis. The method used to determine the acid dissociation constants has been described previously.[5] Equilibrium constants were determined from the absorption spectra of equilibrated solutions and solutions of the pure components, 330–720 nm, as previously described.[13] Rate constants were determined by minimization of

$$\sum_\lambda \sum_t [(A(\lambda,t)_{obs}-A(\lambda,t)_{calc})^2/\sigma^2(A(\lambda,t)_{obs})]$$

where $A(\lambda,t)_{obs}$ and $\sigma(A(\lambda,t)_{obs})$ is the absorbance and standard deviation upon the absorbance at wavelength λ and at time t, and

$$A(\lambda,t)_{calc}=A_o(\lambda)+A_1(\lambda) \exp (-kt)$$

The minimization was carried out as function of k, $A_o(\lambda)$ and $A_1(\lambda)$. The large number of parameters for the multi wavelength experiments were handled by the method described earlier.[14]

In the final calculations which gave the parameters in Table 2,

$$\sum[(\kappa_{obs}-\kappa_{calc})^2/\sigma^2(\kappa)]$$

with $\kappa=K_X$, K_A or k, *cf.* eqns. 2−4, was minimized as function of the parameters in this table.

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