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Kinetics and Mechanism of Ligand Substitution in Some Chromium(III) Tetraaza Macrocyclic Complexes in Acidic Media: Differences in Reactivity Between *cis* and *trans* Isomers

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Thiocyanate anation of the macrocyclic complexes *cis*-$[Cr(cyc\textit{b})(OH_2)_2]^{3+}$ and *trans*-$[Cr(cyc\textit{a})(OH_2)_2]^{3+}$ (cyc*b* and cyc*a* are *rac*- and *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, respectively), and mercury(II)-induced aquation of the product thiocyanato-*N* complexes, has been studied in acidic solution. The rate retardation with an increase of the acid concentration for both types of reactions follows the rate expression $k_{obs} = (k_1 + k_2K_a/[H^+_{(aq)}])/(1 + K_a/[H^+_{(aq)}])$, corresponding to parallel reaction paths through aqua and hydroxo complexes. Some general trends in the differences in reactivity between the two geometrical isomers have been observed and are discussed.

Introduction

Recent advances in the elucidation of the mechanisms of ligand-substitution reactions in solution have been reviewed in a series of articles.[1] The chemistry of transition metal complexes of macrocyclic ligands is an area that has attracted considerable interest in recent years.[2–6] These complexes exhibit a range of characteristic properties that are frequently so markedly different from those of their acyclic analogues that the special, but not very informative, label "macrocyclic effects" has been introduced to describe the differences.

Cyclic tetraaza ligands are among the more readily available macrocyclic ligands, and these ligands have been coordinated to most metal ions of the periodic table. Macrocyclic ligands are usually robustly bound, even to metal ions otherwise characterized as "labile", but knowledge of their ability to modify reactivities at the coordination positions not occupied by the macrocyclic ligand is very sparse for most metal ions.

Base hydrolysis of *cis*-$[Cr(cyc\textit{b})(OH)X]^+$- and *trans*-$[Cr(cyc\textit{a})(OH)X]^+$-type species ($X^- = Cl^-$, NCS^-, or N_3^-), leading to liberation of the X ligand and formation of the dihydroxo complexes, has been studied previously.[7] These processes occur without any stereochemical changes or aquation of the macrocyclic amine ligand, even at higher temperatures and in strongly basic solution. However, they are markedly influenced by the composition of the ionic medium, and this has been rationalized by a competitive ion-pair formation between hydroxide ions and the anion of the supporting electrolyte.

The aim of the present work is to gain further insight into the mechanism of ligand substitution in this type of complexes in acidic media by comparison of the reactivity of the two geometrical isomers in two types of reactions, namely anation of the diaqua complexes *cis*-$[Cr(cyc\textit{b})(OH_2)_2]^{3+}$ and *trans*-$[Cr(cyc\textit{a})(OH_2)_2]^{3+}$ by thiocyanate and mercury(II)-induced aquation of the thiocyanato ligand by formation of the heterodinuclear ions *cis*-$[(cyc\textit{b})(H_2O)Cr\text{-}NCS\text{-}Hg]^{4+}$ and *trans*-$[(cyc\textit{a})(H_2O)Cr\text{-}NCS\text{-}Hg]^{4+}$.

Results and Discussion

Characteristics of the Systems Studied

Direct structural investigations on chromium(III) complexes of the ligands cyc*a*[8] and cyc*b*[9] (Scheme 1), as well as other types of evidence, point towards structures of the diaqua complexes with two equivalent water ligands. Consequently, substitution of a water ligand with another monodentate ligand will give only one product. For the thiocyanato ligand, this has previously been demonstrated by isolation of solutions of aquathiocyanato-type complexes formed by thiocyanate anation of *cis*-$[Cr(cyc\textit{b})(OH_2)_2]^{3+}$ and *trans*-$[Cr(cyc\textit{a})(OH_2)_2]^{3+}$, in which only one isomer was present.[7]

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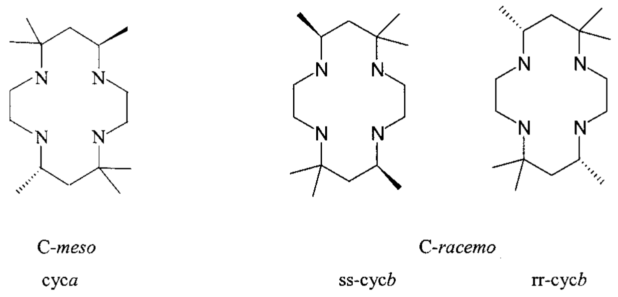


Scheme 1.

The thiocyanato ligand in these complexes is sufficiently robustly coordinated for complexation of mercury(II) to the uncoordinated sulfur atom of the thiocyanato ligand to be studied free from complications due to aquation of this ligand. Preliminary results demonstrated that anation of the diaqua complexes by thiocyanate and mercury(II)-assisted aquation of the monothiocyanato-*N* derivatives proceed, for both the macrocyclic ligands studied, according to Equations (1) and (2):

$$[\mathrm{Cr(cyc)(OH_2)_2}]^{3+} + \mathrm{NCS^-} \rightarrow [\mathrm{Cr(cyc)(OH_2)(NCS)}]^{2+} + \mathrm{H_2O} \quad (1)$$

$$[\mathrm{Cr(cyc)(OH_2)(NCS)}]^{2+} + \mathrm{Hg^{II}} + \mathrm{H_2O} \rightarrow [\mathrm{Cr(cyc)(OH_2)_2}]^{3+} + \mathrm{Hg(SCN)^+_{aq}} \quad (2)$$

Complete retention of configuration is observed in these reaction sequences and the possible aquation of the macrocyclic ligand does not interfere with the reactions under the conditions applied in the present work. This conclusion is based on the results of chromatographic separations and electronic spectra of the eluted chromium(III) species.

The value of the formation constant, at 298 K, for mercury(II) complexation to cationic complexes is usually between 10^3 and 10^4 $\mathrm{M^{-1}}$, and for complexation to anionic complexes usually somewhat higher[10,11] (frequently over 10^5 $\mathrm{M^{-1}}$). The values found for the present cationic macrocyclic complexes (Table 1) are similar, 3.9×10^3 $\mathrm{M^{-1}}$ for the *trans* and 8.5×10^3 $\mathrm{M^{-1}}$ for the *cis* isomer. The complexation reactions are both significantly exothermic (with small negative entropies of reaction), as expected for the interaction between a "soft" metal center and a "soft" ligand.

The macrocyclic chromium(III) complexes were further characterized by their acid/base properties; the acidity constants determined for the aquathiocyanato and the diaqua complexes are presented in Table 2. It can be seen that the acidity constants for the monothiocyanato 2+ complexes are over one order of magnitude lower than those of the diaqua 3+ complexes, which is as expected from the overall charge variation of the complexes. A direct titrimetric determination of the acidity constants for the dinuclear Cr–NCS–Hg^{4+} species was not possible because of the need for a large excess of mercury(II), which exhibits similar acid/base properties to the investigated complexes.[12] In the hydrogen concentration range selected for kinetic measurements, deprotonation of the aqua complexes is stoichiometrically unimportant.

Kinetics of the Mercury(II)-Induced Aquation Reaction

Mercury(II) aquaion is known to efficiently induce aquation of both halide and pseudo-halide ligands in robust classical complexes[13] as well as in organometallic species.[14] A rate enhancement of up to four orders of magnitude[10,11] has been observed for thiocyanato ligand aquation due to coordination of mercury(II) to the uncoordinated sulfur atom of this ligand. Examples are known, however, of mercury(II) causing rate retardation by coordination at another available position and not at the ligand which is the leaving group.[15]

The mercury(II)-induced aquation reactions of the present macrocyclic complexes have been studied in the presence of an excess of mercury(II) sufficient to transform the aquathiocyanatochromium(III) reagents into [Cr^{III}–NCS–Hg^{II}]-type complexes with a degree of conversion exceeding 95%. This guarantees independence of the observed rate constant on the mercury(II) concentration. The two macrocyclic thiocyanatochromium(III) complexes aquate, with a rate that decreases with an increase in acid concentration, as shown in Figure 1.

Table 1. Equilibrium constants (K_{Hg} at 298 K) and reaction enthalpies ($\Delta_r H°$) for mercury(II) complexation to aquathiocyanato complexes of two macrocyclic chromium(III) complexes in 2.0 M (Na/H)ClO$_4$. Standard deviations are given in parentheses.

Chromium(III) complex	K_{Hg} (298 K) [$\mathrm{M^{-1}}$]	$\Delta_r H°$ [kJ mol^{-1}]	$\Delta_r S°$ [J K^{-1} mol^{-1}]
trans-[Cr(cyc*a*)(OH$_2$)(NCS)]$^{2+}$	$3.90(10) \times 10^3$	–28.5(10)	–27(3)
cis-[Cr(cyc*b*)(OH$_2$)(NCS)]$^{2+}$	$8.5(2) \times 10^3$	–25.0(10)	–9(3)

Table 2. Acidity constants, K_{a1}, for monoaqua complexes at 298 K and 313 K, K_{a1} and K_{a2} for diaqua complexes at 298 K, and reaction enthalpies, $\Delta_r H°$, determined by acid/base titrations in 1.0 M NaBr. Standard deviations are given in parentheses.

Complex	–log(K_a/M) (298 K)	–log(K_a/M) (313 K)	$\Delta_r H°$ [kJ mol^{-1}]
trans-[Cr(cyc*a*)(OH$_2$)$_2$]$^{3+}$	2.44(3) 6.929(12)		29(8) 38(2)
trans-[Cr(cyc*a*)(OH$_2$)(NCS)]$^{2+}$	3.817(8)	3.70(4)[a]	24(3)
cis-[Cr(cyc*b*)(OH$_2$)$_2$]$^{3+}$	3.490(8) 7.112(6)		29.4(10) 41.7(13)
cis-[Cr(cyc*b*)(OH$_2$)(NCS)]$^{2+}$	5.298(5)	4.91(2)[a]	30(7)

[a] Noticeable decomposition during titration. The $\Delta_r H°$ values given are those from Table 4.

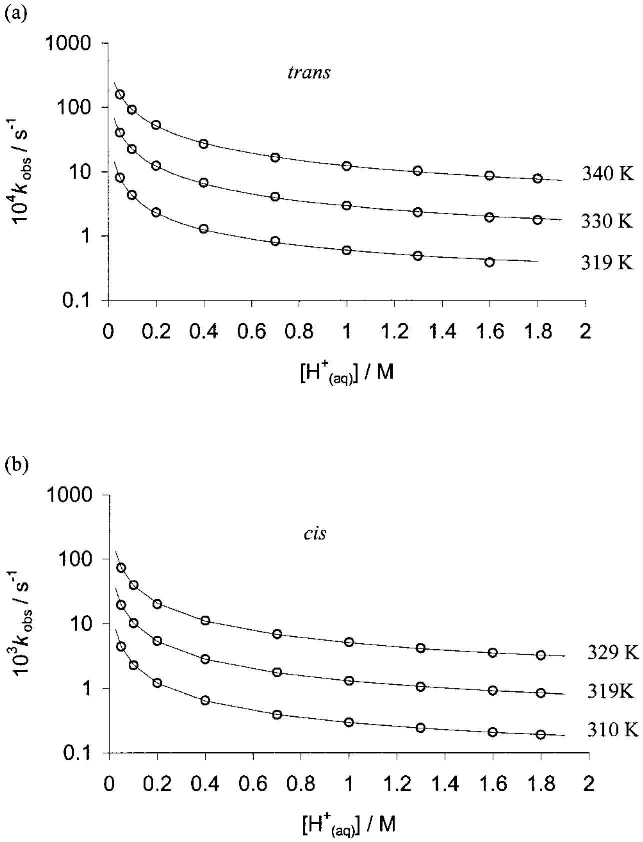
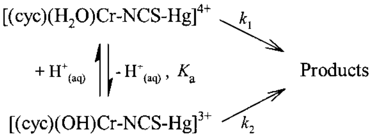


Figure 1. Pseudo-first-order rate constants for aquation of *trans*-$[(cyc\textit{a})(H_2O)Cr\text{-}NCS\text{-}Hg]^{4+}$ (a) and *cis*-$[(cyc\textit{b})(H_2O)Cr\text{-}NCS\text{-}Hg]^{4+}$ (b) complexes as a function of the hydrogen ion concentration in 2.0 M $(H/Na)ClO_4$; $[Hg^{II}]$ = 25 mM.

The observed pseudo-first-order rate constant, k_{obs}, vs. $[H^+_{(aq)}]$ data can be reproduced by Equation (3) which is derived by assuming a fast protolytic equilibrium step followed by the parallel substitution of the thiocyanato-*S*–mercury(II) ion from the aqua and the hydroxo forms of the reagents, as shown in Scheme 2.

$$k_{obs} = (k_1 + k_2{\cdot}K_a/[H^+_{(aq)}])/(1 + K_a/[H^+_{(aq)}]) \qquad (3)$$



Scheme 2.

Non-linear regression analysis was used to give the parameters in Table 3. The data in this table show that the values of the rate constants and the acid dissociation constants are obtained with significant errors despite the good fit of the data to the theoretical equation. This is mainly caused by the relatively narrow range of hydrogen ion concentrations that had to be used.

The values of the acidity constants, K_a, for both isomers of $[Cr(cyc)(H_2O\text{–}NCS\text{–}Hg)]^{4+}$-type (see Table 3) seem to be reasonable and are remarkably higher than those for the $[Cr(cyc)(H_2O)(NCS)]^{2+}$-type isomers (Table 2), as can be expected due to the higher charge of the cationic complexes. However, the acidity constants for the *trans*- and *cis*-thiocyanato ions differ significantly (about 30 times), whereas the values for the mercury(II) derivatives are very similar.

The reactivity comparison of the *cis* and the *trans* isomers in the aqua (k_1) and hydroxo (k_2) forms is based on the two parameters in Equation (3). The k_1 and k_2 values at 298 K for the *cis* isomer are about 20 times higher than for the *trans* one in spite of the higher value of the activation energy. The k_2/k_1 quotient is a measure of the labilizing effect of OH^- *trans* and *cis* to the leaving ligand. These values are similar for both isomers — about 1330 for the *cis* and about 1000 for the *trans* species. The rate constant increase due to deprotonation of the coordinated water molecule is larger for the studied macrocyclic complexes than for many other chromium(III) complexes; $[Cr(H_2O)_5(OH)]^{2+}$, for example, exchanges its water molecule only 75 times faster than $[Cr(H_2O)_6]^{3+}$.[1] The significant uncertainties in the activation parameters make mechanistic con-

Table 3. Rate constants (k_1 and k_2 at 298 K and 323 K), acidity constants (K_a at 298 K and 323 K), activation energies (E_a) and reaction enthalpies ($\Delta_rH°$) for mercury(II)-induced aquation of two macrocyclic chromium(III) complexes in 2.0 M $(Na/H)ClO_4$ [see Scheme 2 and Equation (3)]. Standard deviations are given in parentheses.[a]

trans-$[Cr(cyc\textit{a})(OH_2)(NCS)]^{2+}$	298 K	323 K	E_a or $\Delta_rH°$ [kJ mol^{-1}]
k_1 [s^{-1}]	$6(2) \times 10^{-7}$	$2.0(2) \times 10^{-5}$	113(11)
k_2K_a [M^{-1} s^{-1}]	$1.19(2) \times 10^{-6}$	$8.5(2) \times 10^{-5}$	137(2)
k_2 [s^{-1}]	$6(2) \times 10^{-4}$	$9.9(12) \times 10^{-3}$	89(8)
–log(K_a/M)	2.72(18)	2.06(6)	48(9)
cis-$[Cr(cyc\textit{b})(OH_2)(NCS)]^{2+}$	298 K	323 K	E_a or $\Delta_rH°$ [kJ mol^{-1}]
k_1 [s^{-1}]	$9.8(6) \times 10^{-6}$	$4.66(12) \times 10^{-4}$	124(2)
k_2K_a [M^{-1} s^{-1}]	$3.42(6) \times 10^{-5}$	$1.831(13) \times 10^{-3}$	127.5(7)
k_2 [s^{-1}]	$1.3(2) \times 10^{-2}$	$4.4(3) \times 10^{-1}$	114(7)
–log(K_a/M)	2.57(9)	2.38(3)	14(8)

[a] It should be noted that the functional form of the mathematical equation used to interpret the data does not allow a particularly well-defined separation of the k_2 and the K_a parameters for the present set of data. Consequently, the significantly better defined parameter product k_2K_a is also given in the table.

siderations difficult, although the rate enhancement is accompanied by a lowering of the activation energy (Table 3) rather than the increase observed if the mechanism changes from I_a to I_d as the result of the deprotonation. Remarkably, the k_1 rate constants for the studied macrocyclic complexes are three to four orders of magnitude lower than those for other Cr^{III}–NCS–Hg type species that are thought to be very inert.[10,11] Thus, the "kinetic macrocyclic effect" manifests itself first of all in the extreme inertness of both geometrical isomers and in a strong reactivity difference between the aqua and the hydroxo forms of the complexes.

Kinetics of the Anation Reaction

Both *cis*-$[Cr(cyc\mathit{b})(OH_2)_2]^{3+}$ and *trans*-$[Cr(cyc\mathit{a})(OH_2)_2]^{3+}$ isomers undergo slow anation by thiocyanate in acidic media to give the corresponding monothiocyanato complexes. At lower temperatures — 298–318 K for the *cis* and 308–328 K for the *trans* complex — the reaction is so slow that it can be conveniently studied by applying an initial rate analysis. The pseudo-zero-order rate constants, $k^{(0)}$, were found to be proportional to the chromium(III) concentration, and were converted to pseudo-first-order rate constants, $k^{(1)}$, with [Equation (4)].

$$k^{(1)} = k^{(0)}/[Cr^{III}] \tag{4}$$

These constants depend on the thiocyanate and hydrogen ion concentrations, as demonstrated in Figures 2 and 3. For thiocyanate concentrations below 0.1 M, the pseudo-first-order rate constant is proportional to the thiocyanate concentration, whereas at higher thiocyanate concentrations a non-linear behaviour is seen. In the simple anation model two parameters — the encounter complex formation constant Q and the rate constant k — describe the reaction of a particular reagent. However, the non-linear kinetics of the reaction observed at higher NCS^- concentration (Figure 3) does not allow for the separation of these parameters and are ignored in the following discussion.

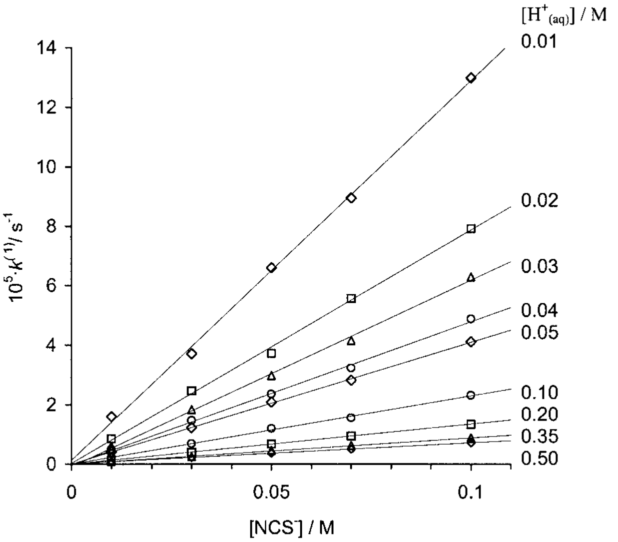


Figure 2. Pseudo-first-order rate constants for anation of *cis*-$[Cr(cyc\mathit{b})(H_2O)_2]^{3+}$ as a function of the thiocyanate concentration in 1.0 M (H/Na)(Br/NCS); T = 298 K.

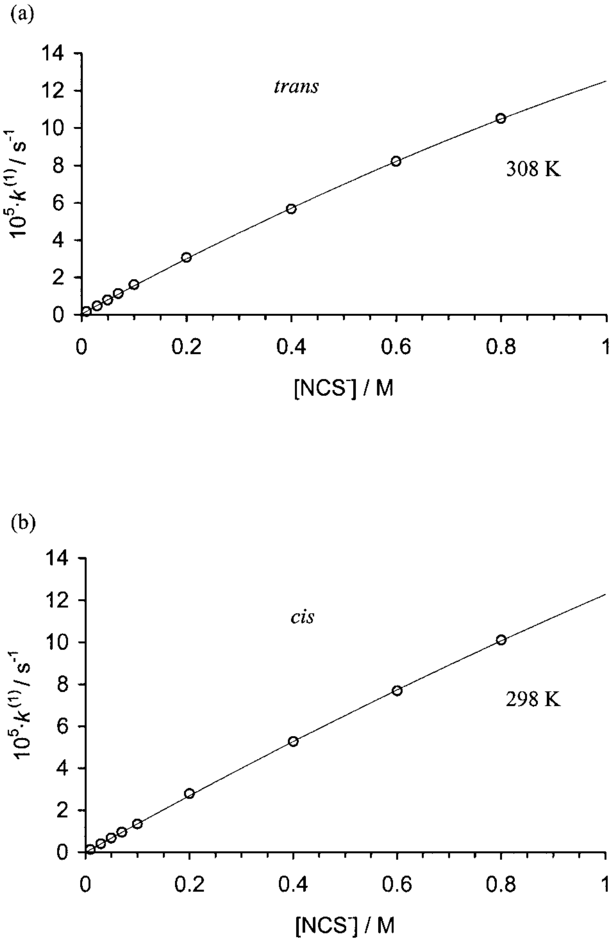


Figure 3. Pseudo-first-order rate constants for anation of *trans*-$[Cr(cyc\mathit{a})(H_2O)_2]^{3+}$ (a) and *cis*-$[Cr(cyc\mathit{b})(H_2O)_2]^{3+}$ (b) as a function of the thiocyanate concentration in 1.0 M (H/Na)(Br/NCS); $[H^+_{(aq)}]$ = 0.2 M.

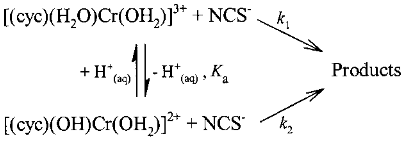
At higher temperatures — 318–338 K for the *cis* and 328–348 K for the *trans* complex — reactions were monitored under pseudo-first-order conditions with thiocyanate in substantial excess over the chromium(III) reagent. Under such conditions the reactions are of first order, and the pseudo-first-order rate constant is proportional to the thiocyanate concentration, in agreement with the results at lower temperatures. Ignoring the data demonstrating deviations from linearity at thiocyanate concentrations higher than 0.1 M, the reactions are found to be of second order, first order in complex and first order in thiocyanate, corresponding to the second-order anation rate constant, k_{an}, given by Equation (5) where k_{an} can be interpreted, in terms of a simple anation model, as the product of the encounter complex formation constant Q and the rate constant k [Equation (6)] if the pre-equilibrium step is shifted to the left.

$$k_{an} = k^{(1)}/[\mathrm{NCS}^-] \quad (5)$$

$$\text{M-OH}_2 + \text{X} \underset{}{\overset{Q}{\rightleftharpoons}} \text{MOH}_2,\text{X} \xrightarrow{k} \text{MX} \quad (6)$$

The hydrogen ion concentration dependence of the second-order rate constant is shown in Figure 4. The significant rate retardation at high acidities can be rationalized in terms of the reaction given in Scheme 3, which shows parallel reaction paths by water ligand substitution in the diaqua and the aquahydroxo complexes and gives the expression in Equation (7) for the second-order anation rate constant.

$$k_{an} = (k_1 + k_2 \cdot K_a/[\mathrm{H}^+_{(aq)}])/(1 + K_a/[\mathrm{H}^+_{(aq)}]) \quad (7)$$



Scheme 3.

The parameters obtained by combining the rate data for all the kinetic experiments are given in Table 4. The validity of the proposed reaction scheme can be verified by comparison of the kinetically determined acidity constants, K_a, with those determined independently by titration experiments (see Table 2). A very good agreement of these two sets of parameters supports the correctness of the postulated reaction model.

The data in Table 4 show that, as in the case of the aquation, the values of the rate constants and the acid dissociation constants have been determined with significant errors.

The results obtained for the anation demonstrate, as for the aquation, a higher reactivity of the *cis* isomer; the ratio of k_1 for the *cis* and *trans* isomers is about 7 whereas the same ratio for k_2 is even higher at about 380. Deprotonation of the coordinated water molecule increases the reactivity, as in the case of the aquation, although the extent of this effect is different for the isomers: the k_2/k_1 quotient is about 1100 for the *cis* but only around 20 for the *trans* isomer. However, it should be noted that the k_1 and k_2 parameters are composite quantities, interpreted in terms of a simple

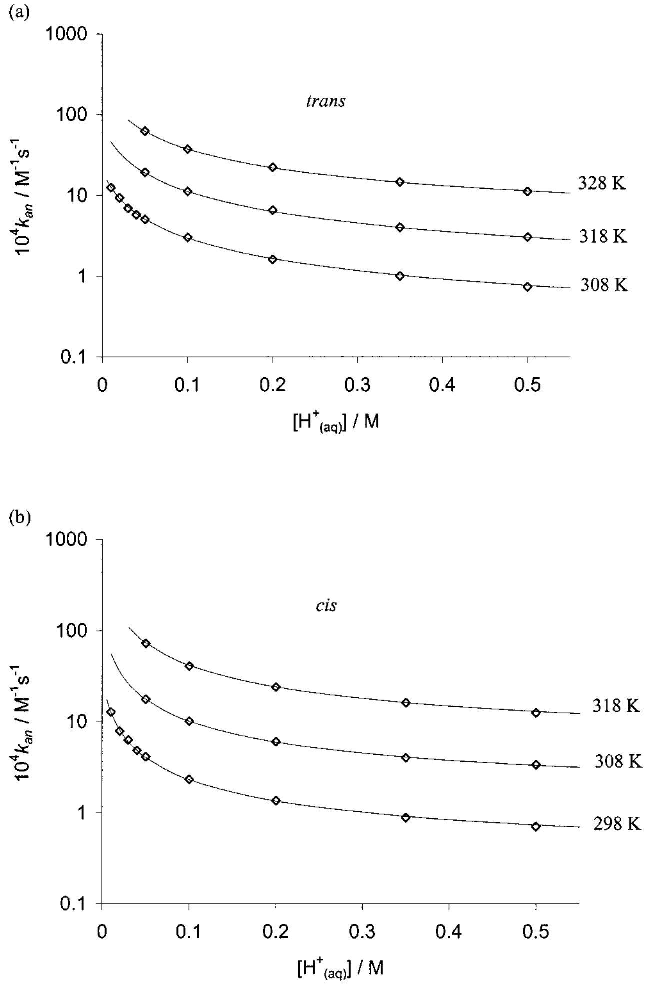


Figure 4. Pseudo-second-order rate constants for the anation of *trans*-[Cr(cyc*a*)(H$_2$O)$_2$]$^{3+}$ (a) and *cis*-[Cr(cyc*b*)(H$_2$O)$_2$]$^{3+}$ (b) complexes by NCS$^-$ as a function of [H$^+_{(aq)}$]; I = 1.0 M (H/Na)(Br/NCS).

Table 4. Rate constants (k_1 and k_2 at 298 K and 323 K), acidity constants (K_a at 298 K and 323 K), activation energies (E_a) and reaction enthalpies ($\Delta_rH°$) for thiocyanate anation of two macrocyclic chromium(III) complexes in 1.0 M (Na/H)(Br/NCS) [see Scheme 3 and Equation (7)]. Standard deviations are given in parentheses.[a]

trans-[Cr(cyc*a*)(OH$_2$)$_2$]$^{3+}$	298 K	323 K	E_a or $\Delta_rH°$ [kJ mol^{-1}]
k_1 [s^{-1}]	$6.5(9) \times 10^{-6}$	$2.61(18) \times 10^{-4}$	119(6)
k_2K_a [M^{-1} s^{-1}]	$4.92(14) \times 10^{-6}$	$2.42(4) \times 10^{-4}$	124.9(8)
k_2 [s^{-1}]	$1.25(6) \times 10^{-3}$	$2.95(8) \times 10^{-2}$	101.3(12)
–log(K_a/M)	2.40(3)	2.084(16)	23.6(15)
cis-[Cr(cyc*b*)(OH$_2$)$_2$]$^{3+}$	298 K	323 K	E_a or $\Delta_rH°$ [kJ mol^{-1}]
k_1 [s^{-1}]	$4.2(3) \times 10^{-5}$	$9.4(11) \times 10^{-4}$	100(5)
k_2K_a [M^{-1} s^{-1}]	$1.73(5) \times 10^{-5}$	$9.38(13) \times 10^{-3}$	128.0(8)
k_2 [s^{-1}]	$4.8(11) \times 10^{-2}$	1.03(8)	98(7)
–log(K_a/M)	3.44(11)	3.04(4)	30(8)

[a] It should be noted that the functional form of the mathematical equation used to interpret the data does not allow a particularly well-defined separation of the k_2 and the K_a parameters for the set of data for the *cis* isomer. Consequently, the significantly better defined parameter product k_2K_a is also given in the table.

anation model, as the product of the encounter complex formation constant Q and the rate constant k [see Equation (6)].

The significant uncertainties in the apparent activation parameters for the anation make them almost unusable for mechanistic considerations.

Summary and Conclusions

Data for the presently investigated reactions, supplemented with base hydrolysis data for complexes of the same macrocyclic ligands,[7] are shown in the form of a linear free energy relationship at 298 K in Figure 5. The same trend in the relative rates is observed for the *cis* and the *trans* series of complexes, with the *trans* complexes reacting between 6.5 and 38 times slower than the *cis* complexes. The linearized correlation in Figure 5 corresponds to the rate constant relationship $k_{cis} \approx 20 k_{trans}$, or to a difference in the free energy of activation of about 8 kJ mol^{-1}. Regrettably, the activation parameters are not accurate enough to separate the free energy into well-defined enthalpy and entropy contributions.

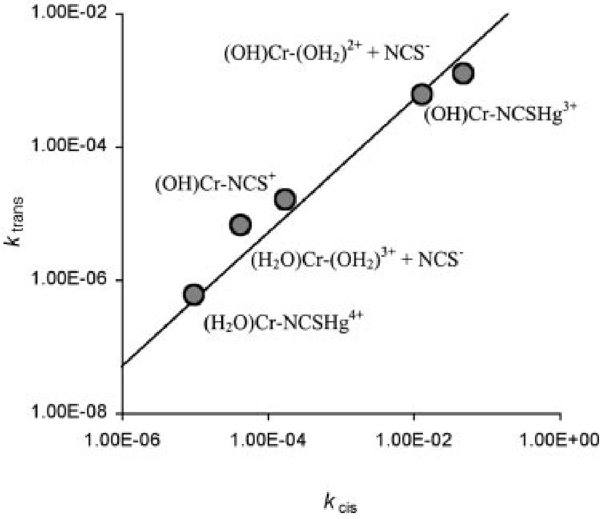


Figure 5. Correlation between free energies of activation for reactions of *cis*-Cr(cyc*b*) and *trans*-Cr(cyc*a*) complexes at 298 K. The data are from this work and from ref.[7] Rate constants are given in units of s^{-1} or M^{-1} s^{-1} according to the type of reaction. The line drawn corresponds to $k_{cis} \approx 20 k_{trans}$.

Some other general trends are worth pointing out explicitly. For example, the exceptional inertness and stereorigidity is a characteristic feature of the studied macrocyclic complexes. An increased acidity of the water ligands coordinated to the macrocyclic complexes with a highly hydrophobic coordination sphere is also seen. For the present complexes, this manifests itself in dominating reactivity contributions from deprotonated complexes, even in strongly acidic solution. The strong increase in reactivity caused by the coordinated water molecule deprotonation may be correlated with a lowering of the energy of activation. Regrettably, however, the present data are not accurate enough to determine whether this is the only effect operating. This effect is practically non-directional for the aquation but, unexpectedly, is much stronger in the *cis* position for the anation. The general reactivity pattern of the present reactions follows that normally seen for complexes of chromium(III) involving slow substitution processes of and by thiocyanate ligands.

Experimental Section

Materials: *cis*-[Cr(cyc*b*)(OH$_2$)$_2$]Br$_3$·2H$_2$O was prepared according to a literature method;[16] *trans*-[Cr(cyc*a*)(OH$_2$)$_2$]Br$_3$·3H$_2$O was prepared analogously;[16] *cis*-[Cr(cyc*b*)(OH$_2$)(NCS)]$^{2+}$ and *trans*-[Cr(cyc*a*)(OH$_2$)(NCS)]$^{2+}$ complexes were prepared and characterised in solution as described previously.[7] Sephadex SP C-25 (Na$^+$,H$^+$) was used for chromatographic separations. Other chemicals were the best available commercial grades. For all solutions doubly distilled water was used.

Determination of the Formation Constant for the Cr^{III}–NCS–Hg^{II} Complexes: Equilibrium constants, K_{Hg}, for reactions of the type shown in Equation (8) were determined spectrophotometrically at λ = 312 nm for the *cis* isomer and at λ = 309 nm for the *trans* isomer, using a Perkin–Elmer Lambda-20 spectrophotometer.

$$[Cr(cyc)(OH_2)(NCS)]^{2+}{}_{(aq)} + Hg^{2+}{}_{(aq)} \rightleftharpoons [Cr(cyc)(OH_2)(NCS\text{-}Hg)]^{4+}{}_{(aq)} \quad (8)$$

Spectra were taken immediately after mixing of the reactants, and effects of subsequent aquation reactions were not observed during the time of the experiments. A decrease of the thiocyanatochromium(III) charge-transfer bands with an increase of the mercury(II) concentration was observed for both isomers. An example is shown in Figure S1 (see Supporting Information). The equilibria in Equation (8) were examined at three temperatures (293.7–330.1 K) at a hydrogen ion concentration of 0.5 M and an ionic strength of 2.0 M maintained by the addition of NaClO$_4$. The concentration of the chromium(III) species was about 0.4 mM and the mercury(II) concentration was varied between 0.1 and 2.5 mM. The equilibrium constants, K_{Hg}, were calculated from Equation (9) which is derived from the relevant mass-action expressions in Equation (10) where [C] = [S] + [P], P = [Cr(cyc)(OH$_2$)(NCS–Hg)]$^{4+}{}_{(aq)}$, S = [Cr(cyc)(OH$_2$)(NCS)]$^{2+}{}_{(aq)}$, [P] = $(A_i - A_s)/\Delta\varepsilon$, $\Delta\varepsilon = \varepsilon_p - \varepsilon_s$, assuming ε_p = 0. The results are given in Table 1.

$$A_i = \frac{[Hg^{2+}_{(aq)}]_i\,\varepsilon_s K_{Hg} + A_s K_{Hg} + \varepsilon_s + \sqrt{K_{Hg}^{2}([Hg^{2+}_{(aq)}]_i\,\varepsilon_s + A_s)^2 + 2K_{Hg}([Hg^{2+}_{(aq)}]_i\,\varepsilon_s^2 - A_s\varepsilon_s) + \varepsilon_s^2}}{2K_{Hg}} \quad (9)$$

$$K = \frac{[P]}{([C]-[P])([Hg^{2+}_{(aq)}]_i - [P])} \qquad (10)$$

Identification of Reaction Products: Stoichiometric studies of the aquation of the Cr^{III}–NCS–Hg^{II} complexes were carried out to 95% conversion and anation of the diaqua isomers by thiocyanate to 5% conversion. The reaction mixtures were chromatographed and the chromium(III) species were eluted with 0.1–0.5 M $HClO_4$. The complexes were identified by their UV/Vis spectra. Chromium concentrations were determined by atomic absorption spectrometry using a Varian ABQ-20 instrument.

Mercury(II)-Assisted Aquation Kinetics: These reactions were monitored spectrophotometrically using a Shimadzu UV-1601 PC spectrophotometer equipped with a Shimadzu CPS-240A digital temperature controller. Absorbance/time data were collected at λ = 270 nm for the *cis* isomer and at λ = 265 nm for the *trans* isomer; the decrease of absorbance was up to 0.4. The kinetic experiments covered the temperature range 298–329 K for the *cis* and 298–340 K for the *trans* isomer and the hydrogen ion concentration range 0.02–1.8 M, giving half-lives of the reactions of between 6 and 18000 s. The chromium(III) concentration was kept at 0.25 mM in most of the experiments but was varied in the range 0.2–0.5 mM. The concentration of mercury(II) necessary for greater than 95% transformation of the starting complexes into the dinuclear compounds was kept at 25 mM in most experiments but was varied in the concentration range 0.02–0.1 M. The ionic strength was maintained constant at 2.0 M by the addition of $NaClO_4$. Reactions were initiated by injecting a portion of the stock complex solution (0.2 mL) into a thermostatted solution (1.8 mL) containing all other components. Kinetic runs were repeated three times, five times at the lowest $H^+_{(aq)}$ concentration. The pseudo-first-order rate constants, k_{obs}, were calculated by standard non-linear regression analysis from the absorbance, A_{obs}, vs. time, t, data using the formula $A_{obs} \approx A_{calc} = A_0 + A_1 \cdot e^{-k_{obs} \cdot t}$. Data up to four half-lives were used for the rate-constant calculations. The obtained rate constants were practically independent of the chromium(III) concentration and independent of mercury(II) concentrations at levels above 0.02 M. The average reproduction in the final calculations to give the rate constants and activation parameters of Table 3 was about 1.0% for the *cis* reagent and 3.6% for the *trans* reagent.

Thiocyanate Anation Kinetics: The thiocyanate anation reactions were monitored spectrophotometrically at λ = 310 nm using Perkin–Elmer Lambda 18 and Lambda 20 spectrophotometers, with cell holders thermostatted with a Perkin–Elmer or a Julabo F-25 thermostat. The ionic strength was kept constant at 1.0 M with H^+, Na^+, Br^- and NCS^-. Kinetic measurements at the lower temperatures were done by applying an initial rate method, under pseudo-zero-order conditions, where the increase of absorbance was recorded up to less than 5% of the conversion degree. Absorbance changes for the *trans* isomer are shown in Figure S2 in the Supporting Information. The absorbance changes for the *cis* complex are analogous to those seen for the *trans* complex, as could be expected. The experiments covered the temperature range 298–318 K for the *cis* and 308–328 K for the *trans* complex and the concentration ranges $[Cr^{III}]$ = 5–15 mM, $[NCS^-]$ = 0.01–0.8 M and $[H^+_{(aq)}]$ = 0.01–0.5 M. The reactions were initiated by injection of a stock NaNCS solution (0.1 mL) into a thermostatted solution (1.9 mL) containing all other components. All kinetic runs were repeated three times. The pseudo-zero-order rate constants, $k_{obs}^{(0)}$, were calculated by linear regression analysis from the absorbance, A, vs. time, t, data using the expression $A_{obs} \approx A_{calc} = A_0 + k_{obs}^{(0)} \cdot \varepsilon_{310} \cdot t$, where ε_{310} is the molar absorption coefficient for the complexes. The pseudo-first-order rate constants $k^{(1)}$, calculated as $k_{obs}^{(0)}/[Cr^{III}] = k^{(1)}$, are directly proportional to the thiocyanate concentration at $[NCS^-] << 0.1$ M. The kinetic parameters obtained in this way are, of course, strongly dependent on the accuracy of the determination of the reactant concentrations and accurate determination of the molar absorption coefficients for the examined complexes. However, a good agreement between the values found by this method at lower temperatures and by the experimental approach described below for the higher temperatures was obtained. Kinetic measurements at these latter conditions were performed under conventional pseudo-first-order conditions with $[Cr^{III}]$ (0.1 mM) << $[NCS^-]$ (0.035–0.1 M). These experiments covered the temperature range 318–338 K for the *cis* and 328–348 K for the *trans* complex and the hydrogen ion concentration range 0.002–0.1 M. The reactions were initiated by injection of a stock solution of the complex (0.1 mL) into a thermostatted solution (3.0 mL) containing all other components. The pseudo-first-order rate constants, $k_{obs}^{(1)}$, were calculated by non-linear regression from the absorbance, A_{obs}, vs. time, t, data using the formula $A_{obs} \approx A_{calc} = A_0 + A_1 \cdot e^{-k_{obs}^{(1)} \cdot t}$. At higher thiocyanate concentrations a deviation from the linear behaviour is seen. The pseudo-first-order rate constants at the lower thiocyanate concentrations were converted into second-order rate constants, and these data are the basis for the average rate constants and activation parameters listed in Table 4. The reproduction of the individual rate constants in this final calculation was about 4.7% for the *cis* reagent and 3.6% for the *trans* reagent.

Determination of Acidity Constants: Acidity constants were determined by potentiometric titrations at 298 and 313 K. The ionic strength was kept constant at 1.0 M by the addition of NaBr. The results are given in Table 2.

Supporting Information (see footnote on the first page of this article): Spectral changes accompanying the addition of mercury(II) to *cis*-$[Cr(cycb)(H_2O)(NCS)]^{2+}$ and anation of *trans*-$[Cr(cyca)(OH_2)_2]^{3+}$ by thiocyanate.

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