# Reaction Rate Studies of the Acid Hydrolysis of Some Chromium-(III) Complexes. VII. The Acid Hydrolysis of Tetraaqua(1,2-ethanediamine)-, Tetraaqua(1,3-propanediamine)- and Tetraaqua-(*trans*-1,2-cyclohexanediamine)chromium(III) Ions in Aqueous Perchloric Acid

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The acid hydrolysis of the diaminetetraaqua-chromium(III) complexes of the three chelating diamines: 1,2-ethanediamine (en), 1,3-propane-diamine (tn) and *trans*-1,2-cyclohexanediamine (chxn) in perchloric acid solution has been investigated in the temperature range 60 – 80 °C and at an ionic strength of 1.0.

For all the complexes the initial hydrolysis reaction produces a monoaminepentaaqua complex with coordinated monodentate protonated diamine. The reaction rate constants at 70 °C and the activation energies were determined to be:[*]

(en): $(11.33 \pm 0.14) \times 10^{-6}$ $s^{-1}$,
25.1 ± 0.4 kcal/mol,
(tn): $(0.650 \pm 0.007) \times 10^{-6}$ $s^{-1}$,
25.9 ± 0.3 kcal/mol,
(chxn): $(6.98 \pm 0.14) \times 10^{-6}$ $s^{-1}$,
27.4 ± 0.8 kcal/mol.

Further hydrolysis of the monoamine complexes yields hexaaquachromium(III) ions, and for these reactions the rate constants at 70 °C and the activation energies were determined to be:

(en): $(5.4 \pm 0.3) \times 10^{-6}$ $s^{-1}$,
29.0 ± 1.6 kcal/mol,
(tn): $(0.66 \pm 0.02) \times 10^{-6}$ $s^{-1}$,
29.7 ± 1.0 kcal/mol,
(chxn): $(18.5 \pm 1.1) \times 10^{-6}$ $s^{-1}$,
28.8 ± 1.6 kcal/mol.

In addition to these acid concentration-independent reactions, the monoamine complex with *trans*-1,2-cyclohexanediamine was found to undergo acid dependent hydrolysis and chelation.

An approximately linear correlation of the logarithm of the rate constants for hydrolysis with the statistically corrected $pK_1$ values for the fully protonated amines is demonstrated for a series of monoaminepentaaquachromium(III) complexes.

A previous qualitative study in this laboratory [1] of the acid hydrolysis of chelated 1,2-ethane-diamine complexes of chromium(III) has demonstrated the similarity of the reaction products in this system and in the chromium-(III) ammonia system. However, the qualitative observations suggested interesting differences in reactivity between analogous complexes in the two systems. The present work therefore describes an extension of earlier quantitative investigations in this laboratory on bond breaking reactions of chromium(III) non-chelated amine complexes to the acid hydrolysis of the symmetrical diamine chelate complexes: tetraaqua(1,3-propanediamine)- and tetraaqua (*trans*-1,2-cyclohexanediamine)chromium(III).

Garner et al.[2] have previously studied the acid-hydrolysis kinetics of the tetraaqua(1,2-ethanediamine)chromium(III) ion in 3 M perchlorate medium. In order to facilitate comparisons with the other diamine system investigated here, the above system has been re-investigated employing a 1 M perchlorate medium.

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[*] 1 kcal = 4.184 kJ.

## EXPERIMENTAL

*Chemicals.** *trans*-[Cr(en)₂(aq)(OH)](ClO₄)₂,[3] *trans*-[Cr(tn)₂(aq)(OH)](ClO₄)₂[4] and *trans*-[Cr((−)ᴅ-chxn)₂F₂]ClO₄[5] were prepared according to literature methods. The latter compound was converted to *trans*-[Cr((−)ᴅ-chxn)₂Cl₂]Cl by reaction with concentrated hydrochloric acid.[3]

*Tetraaqua(1,2-ethanediamine)chromium(III)* and *(2-aminoethylammonium)pentaaquachromium(III) ions.* Both these ions were prepared from trans-aquabis(1,2-ethanediamine)hydroxochromium(III) perchlorate as described previously.[1]

*Tetraaqua(1,3-propanediamine)chromium-(III) ion.* *trans*-Aquahydroxobis(1,3-propanediamine)chromium(III) perchlorate was dissolved in 0.1 M nitric acid and boiled for 30 min. The resulting solution was charged onto a 2 × 5 cm column packed with Dowex 50 W × 8 200/400 mesh cation-exchange resin. Elution with 2 M sulfuric acid produced separation into three bands. From the visible absorption spectra of their eluates these bands were identified as hexaaqua-, tetraaqua(1,3-propanediamine)-, and a mixture of *cis*- and *trans*-diaquabis(1,3-propanediamine)chromium(III), eluted in that order. The eluate of the second band, containing the tetraaqua(1,3-propanediamine)chromium(III) ion in 2 M sulfuric acid, was purified and the sulfate ion exchanged for perchlorate as described earlier.[6]

*(3-Aminopropylammonium)pentaaquachromium(III) ion.* A 0.5 M perchloric acid solution of tetraaqua(1,3-propanediamine)chromium(III), prepared as described above, was kept in the dark at 50 °C for 90 h. The (3-aminopropylammonium)pentaaquachromium(III) ion was isolated from the resulting mixture essentially as described previously for the (2-aminoethylammonium)pentaaquachromium(III) ion.[1]

*Tetraaqua(trans-1,2-cyclohexanediamine)chromium(III) ion.* *trans*-Dichloridobis(*trans*-1,2-cyclohexanediamine)-chromium(III) chloride was boiled for 25 min in 3 M perchloric acid. The resulting mixture was charged onto a 2 × 8 cm column packed with Dowex 50 W × 2 200/400 mesh cation-exchange resin. Elution with 3 M perchloric acid produced separation into three bands. From the visible absorption spectra of the eluates the first band was identified as hexaaqua- and the second as tetraaqua-(*trans*-1,2-cyclohexanediamine)chromium(III).

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* The following ligand name abbreviations are used in chemical formulae throughout the paper: a= ammonia, aq= water, en= 1,2-ethanediamine, enH= 2-aminoethylammonium ion, tn= 1,3-propanediamine, tnH= 3-aminopropylammonium ion, chxn= *trans*-1,2-cyclohexanediamine, chxnH= *trans*-2-aminocyclohexylammonium ion, diam= diamine, diamH= protonated monodentate diamine ion, and diam*= unprotonated monodentate diamine.

The third band, which had a colour characteristic of a tetraaminediaqua complex, was not investigated further. The eluate of the second band, containing the tetraaqua(*trans*-1,2-cyclohexanediamine)chromium(III) ion in 3 M perchloric acid, was purified as described earlier for sulfuric acid eluates.[6]

*(trans-2-Aminocyclohexylammonium)pentaaquachromium(III) ion.* A solution of tetraaqua-(*trans*-1,2-cyclohexanediamine)chromium(III) in 3 M perchloric acid, obtained as described above, was kept in the dark at 70 °C for 18 h. The resulting solution, in which equilibrium between the diamine and monoamine complexes was established, contained mainly unchanged diamine complex and only very little monoamine species. The solution was charged onto a 2 × 4 cm Dowex 50 W × 2 column and eluted with 3 M perchloric acid. The hexaaquachromium(III) ion was eluted first, then the diamine- and finally the monoamine chromium(III) complex.

Because of the large amount of diamine complex necessary to get only small amounts of monoamine complex, it was not possible to separate the diamine, monoamine and hexaaqua complexes completely. The tail of the diamine band (which contained about 75 % of monoamine complex) was therefore recovered, diluted three times with water, re-charged onto a 1 × 5 cm Dowex 50 W × 2 column and re-eluted with 3 M perchloric acid. The two species were not completely separated on this short column but from a fractionation experiment the last part of the band was identified as pure (*trans*-2-aminocyclohexylammonium)pentaaquachromium(III) ion.

Due to fast chelation of the monodentate diamine in this complex at lower acid concentrations it was not possible to purify the solution by the Sephadex technique employed for the other Dowex eluates. In order to get satisfactory absorption spectra, especially in the near-UV region, the Dowex resin was thoroughly washed with a hot mixture of a 0.01 M sodium hydroxide solution and hydrogen peroxide. Prior to the final purification of the (*trans*-2-aminocyclohexylammonium)-pentaaquachromium(III) complex the column was washed first with about 200 ml of water and then with 200 ml of 3 M perchloric acid. The molar absorptivity of the second band of the absorption spectrum was still not quite reproducible and consequently only the first part of the spectra (700 − 470 nm) was used in the kinetic calculations for the experiments starting with the (*trans*-2-aminocyclohexylammonium)chromium(III) ion.

The visible absorption spectra of the 1,2-ethanediamine-, the 1,3-propanediamine-, and the *trans*-1,2-cyclohexanediamine complexes prepared by the above methods are given in Ref. 1 and Figs. 1 and 2.

*Spectral measurements.* All visible absorption spectra were measured on a modified Cary
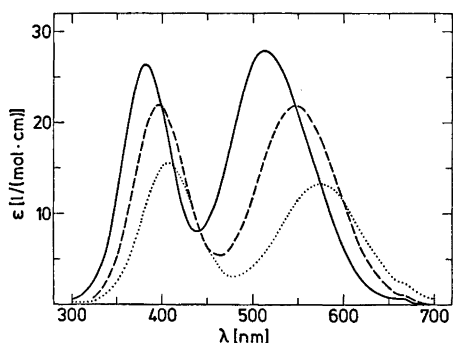
*Fig. 1.* Visible absorption spectra of compounds prepared as described in the text. ———, [Cr(tn)(aq)$_4$]$^{3+}$; —-, [Cr(tnH)(aq)$_5$]$^{4+}$; ···, [Cr(aq)$_6$]$^{3+}$.



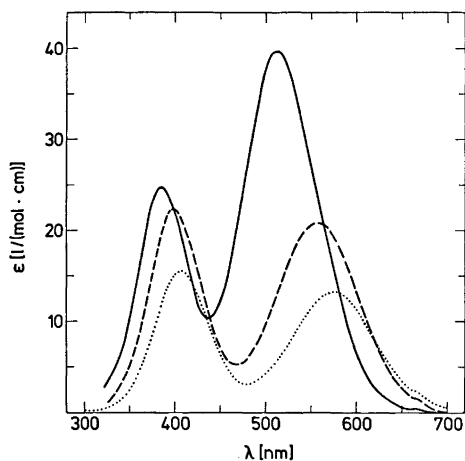*Fig. 2.* visible absorption spectra of compounds prepared as described in the text. ———, [Cr(chxn)(aq)$_4$]$^{3+}$; —-, [Cr(chxnH)(aq)$_5$]$^{4+}$; ···, [Cr(aq)$_6$]$^{3+}$.

118C spectrophotometer at room temperature (23 ± 2 °C).

*Kinetic measurements, determination of chromium and hydrogen ion concentrations, and calculations* were performed essentially as described previously.[6]

*Determination of acidity constants for the free amines.* The diaminedihydrochloride salts in 1.0 M sodium perchlorate solution were titrated at 70 °C with 1 M sodium hydroxide. The titration procedure and the method of calculation have been described earlier.[7] The results are given in Table 1.

*Table 1.* Acidity constants of some protonated amines in 1 M sodium perchlorate solution at 70 °C.

| Amine | pK$_1$ | pK$_2$ |
|---|---|---|
| NH$_3$ | 8.21 ± 0.03 | |
| en | 6.30 ± 0.04 | 9.00 ± 0.02 |
| tn | 7.87 ± 0.03 | 9.48 ± 0.04 |
| chxn | 5.76 ± 0.03 | 8.84 ± 0.03 |

## RESULTS AND DISCUSSION

Acid hydrolysis of *trans*-bis(diamine)chromium(III) species yields large amounts of diaminetetraaquachromium(III) species. This has previously been demonstrated for the 1,2-ethanediamine-[1] and 1,3-propanediamine[4] complexes and is also the case for the *trans*-1,2-cyclohexanediamine complexes. The further hydrolysis of these diamine species proceeds to give the hexaaquachromium(III) ion *via* an intermediate species with coordinated mono-protonated diamine, but unlike the diamine species the monoamine complexes coordinated with monodentate diamines are not present in large amounts.

The hydrolysis of *trans*-diaquabis(1,3-propanediamine)chromium(III) in aqueous perchloric acid is a very slow process. Preparative hydrolysis was therefore carried out in nitric acid since nitrate ions are known to accelerate the hydrolysis of chromium(III) amine complexes.[8] Cation exchange chromatography of the hydrolysed solutions on Dowex × 8 resin with 2 M sulfuric acid resulted in separation into three bands. From the visible absorption spectra of their eluates these bands were identified as hexaaqua-, tetraaqua(1,3-propanediamine)-, and a mixture of *cis*- and *trans*-diaquabis-(1,3-propanediamine)chromium(III) ions.*

* *cis*-Diaquabis(1,3-propanediamine)chromium-(III) prepared by mercury(II) accelerated hydrolysis of *cis*-dichloridobis(1,3-propanediamine)chromium(III) exhibits absorption maxima at 486 nm ($\varepsilon$ 38.8 1/(mol cm)) and 366 nm ($\varepsilon$ 37.9 1/(mol cm)). It therefore appears that an earlier published spectrum[4] of *cis*-diaquabis(1,3-propanediamine)-chromium(III) is, in fact, that of a mixture of the *cis*- and *trans*-diaquabis(1,3-propanediamine)chromium(III) complexes which contains appreciable amounts of the *trans* complex.

Cation exchange chromatography showed that nitric acid hydrolysates of the *trans*-diaquabis(1,3-propanediamine)chromium(III) ion never contained perceptible amounts of tetrapositive species. The (3-aminopropylammonium)pentaaquachromium(III) complex was prepared by heating the tetraaqua(1,3-propanediamine) complex in aqueous perchloric acid at 50 °C for 90 h. This produced a tetrapositive species which was separated from the tripositive species on a SP-Sephadex-C-25 resin column by elution with 0.5 M sodium perchlorate solution. From the mode of formation, the elution behaviour and the visible spectrum this species was identified as the (3-aminopropylammonium)pentaaquachromium(III) ion.

Cation exchange chromatography of a 3 M perchloric acid hydrolysate of *trans*-dichloridobis(*trans*-1,2-cyclohexanediamine)chromium-(III) on Dowex X2 resin produced three bands of tripositive species. From the elution behaviour, the mode of formation and the visible absorption spectra of the eluates, the first and second bands were identified as the hexaaqua- and the tetraaqua(*trans*-1,2-cyclohexanediamine)chromium(III) species, respectively. The third band had a tetraamine colour but was not investigated further.

Ageing of the tetraaqua(*trans*-1,2-cyclohexanediamine)-chromium(III) species in 3 M perchloric acid produced mixtures containing minor amounts of a species which was more difficult to elute from the Dowex X2 resin with

3 M perchloric acid than was the unreacted diamine species. From the mode of formation, the elution behaviour and the visible absorption spectrum this species was identified as the (*trans*-2-aminocyclohexylammonium)pentaaquachromium(III) ion. Attempts at further purification of this species at low acidities ($\sim 0.001$ M) on the Sephadex resin resulted in rapid formation of the tetraaqua(*trans*-1,2-cyclohexanediamine)chromium(III) ion.

In Table 2 the visible absorption spectra of the chromium(III) complexes with the above-mentioned symmetrical diamine ligands are compared with those of the corresponding ammonia complexes. The spectra of the two complexes with a five-membered chelate ring are almost identical and exhibit a molar absorptivity for the first spin allowed absorption band which is substantially larger than that observed for both the tetraaqua(1,3-propanediamine)- and *cis*-diamminetetraaquachromium-(III) ion. However, the three chelate complexes resemble each other in that the first spin allowed absorption band is shifted substantially towards the blue relative to that of the corresponding ammonia complex.

Unlike those of the diamine complexes the spectra of the four monoamine species are seen to resemble each other closely. Neither molar absorptivities nor spectral band maxima vary in an apparently systematic manner. The only noteworthy feature of these data is the significant red-shift of the first spin allowed absorp-

*Table 2.* A comparison of the visible spectra of some symmetrical diaminetetraaquachromium(III)- and of some aminepentaaquachromium(III) complexes.

| Complex | Medium [a] | $\lambda_1$ max nm | $\varepsilon_1$ max l/(mol cm) | $\lambda_2$ max nm | $\varepsilon_2$ max l/(mol cm) | $\varepsilon_1$ max/ $\varepsilon_2$ max | Ref. |
|---|---|---|---|---|---|---|---|
| Diamine complexes | | | | | | | |
| *cis*-[Cr(a)$_2$(aq)$_4$]$^{3+}$ | A | 526 | 27.0 | 386 | 21.3 | 1.27 | 6 |
| [Cr(tn)(aq$_4$]$^{3+}$ | A | 514 | 27.9 | 382 | 26.1 | 1.07 | [b] |
| [Cr(en)(aq)$_4$]$^{3+}$ | B | 512 | 41.3 | 387 | 24.7 | 1.67 | 1 |
| [Cr(chxn)(aq)$_4$]$^{3+}$ | A | 513 | 39.8 | 384 | 24.8 | 1.61 | [b] |
| Monoamine complexes | | | | | | | |
| [Cr(a)(aq)$_5$]$^{3+}$ | A | 547 | 19.9 | 396 | 18.6 | 1.07 | 6 |
| [Cr(tnH)(aq)$_5$]$^{4+}$ | B | 546 | 22.2 | 395 | 22.5 | 0.99 | [b] |
| (Cr(enH)(aq)$_5$]$^{4+}$ | B | 551 | 21.5 | 397 | 21.4 | 1.01 | 1 |
| [Cr(chxnH)(aq)$_5$]$^{4+}$ | C | 556 | 20.6 | 398 | 22.2 | 0.93 | [b] |

[a] A, 0.5 M HClO$_4$ + 0.5 M NaClO$_4$; B, 0.25 M HClO$_4$ + 1.0 M NaClO$_4$; C, 3 M HClO$_4$]. [b] This work.

tion band of the (trans-2-aminocyclohexyl-ammonium)pentaaquachromium(III) species relative to the corresponding band in the other three complexes. Inspection of molecular models reveals the possibility of substantial interaction between the coordinated water molecules and the hydrogen atoms of the cyclohexanediamine ring in this species. This may result in a distorted octahedral structure and thereby rationalise the observed red-shift.

In the qualitative experiments it was found that the diaminetetraaquachromium(III) complexes hydrolyse to hexaaquachromium(III) via monoamine species. It was further found that the amine ligand in the (trans-2-aminocyclohexylammonium)pentaaquachromium(III) complex re-chelates even in weakly acid solution to form the diamine complex. For the (2-aminoethylammonium)triaqua(1,2-ethanediamine)- and the (2-aminoethylammonium)-aquabis(1,2-ethanediamine)chromium(III) complexes similar rechelation reactions were found although these were only observed in basic solution.[1,9]

Calculations for the experiments involving the 1,2-ethanediamine and 1,3-propanediamine complexes were consequently carried out in accordance with the reactions:

$$[Cr(diam) (aq)_4]^{3+} \xrightarrow{k_{21}(obs)} [Cr(diamH) (aq)_5]^{4+}$$
$$\xrightarrow{k_1(obs)} [Cr(aq)_6]^{3+}$$
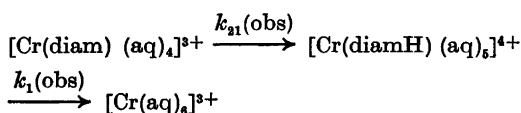
This reaction scheme accurately described our kinetic data, and estimated rate constants for the individual kinetic experiments are tabulated in Table 3. As can be seen from this table the rate constants are independent of the hydrogen ion concentration in the acidity range studied. Average rate constants at 70 °C and activation energies are given in Tables 4 and 5.

In experiments starting from tetraaqua-(trans-1,2-cyclohexanediamine)chromium(III), species coordinated with monodentate diamine were never observed in appreciable amounts. Calculations on the experiments starting with this diaminetetraaqua complex could therefore not be carried out within the framework of a reaction scheme involving an intermediate monoamine species. Consequently the data were parametrised in accordance with the reaction:

$$[Cr(diam) (aq)_4]^{3+} \xrightarrow{k_{20}(obs)} [Cr(aq)_6]^{3+}$$
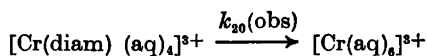
This reaction scheme accurately accommodated the kinetic data, but as shown in Fig. 3 the observed rate constants were dependent on the acid concentration. Such hydrogen ion concentration dependence should be expected if chelation of the diamine ligand in the intermediate monoamine species is important. In order to get further information about the kinetics of this system, experiments with (trans-2-aminocyclohexylammonium)pentaaquachromium(III) as the initial reactant

Table 3. Rate constants and initial complex concentrations calculated for individual kinetic experiments with the chromium(III) complexes of 1,2-ethanediamine and 1,3-propanediamine.

| Run No. | [Cr(III)] (mmol/l) | [H+] (mol/l) | Temp. (°C) | $10^6 \times k_{21}$ (s$^{-1}$) | $10^6 \times k_1$ (s$^{-1}$) |
|---|---|---|---|---|---|
| 1,2-Ethanediamine | | | | | |
| 1[a] | $0.470 \pm 0.003$ | 1.0 | 79.85 | $31.8 \pm 0.6$ | $18.5 \pm 0.9$ |
| 2[a] | $0.470 \pm 0.004$ | 0.5 | 79.85 | $28.9 \pm 0.6$ | $20.8 \pm 1.6$ |
| 3 | $0.918 \pm 0.002$ | 1.0 | 70.20 | $11.77 \pm 0.08$ | $5.58 \pm 0.19$ |
| 4 | $0.474 \pm 0.002$ | 1.0 | 59.65 | $3.56 \pm 0.03$ | $1.41 \pm 0.10$ |
| 5[b] | $0.848 \pm 0.002$ | 0.5 | 79.95 | – | $17.7 \pm 0.3$ |
| 1,3-Propanediamine | | | | | |
| 6 | $1.100 \pm 0.005$ | 1.0 | 80.05 | $1.86 \pm 0.03$ | $2.32 \pm 0.11$ |
| 7 | $0.834 \pm 0.004$ | 1.0 | 70.20 | $0.676 \pm 0.009$ | $0.66 \pm 0.03$ |
| 8 | $1.051 \pm 0.004$ | 0.5 | 70.20 | $0.675 \pm 0.008$ | $0.71 \pm 0.03$ |
| 9 | $0.833 \pm 0.003$ | 1.0 | 59.65 | $0.202 \pm 0.004$ | $0.166 \pm 0.008$ |
| 10 | $1.380 \pm 0.004$ | 1.0 | 59.65 | $0.196 \pm 0.002$ | $0.175 \pm 0.006$ |

[a] These two solutions were prepared from the same stock solution. [b] This run was started with the monoamine complex.

*Table 4.* Rate constants at 70 °C and activation energies for the acid hydrolysis of some tetraaquadiamine-chromium(III) complexes.

| Complex | $10^6 \times k_{21}$ (s⁻¹) | $E_A$ (kcal/mol) | Ref. |
|---|---|---|---|
| *cis*-[Cr(a)₂(aq)₄]³⁺ | $3.39 \pm 0.08$ | $27.0 \pm 0.4$ | 12 |
| [Cr(en)(aq)₄]³⁺ [b] | $11.33 \pm 0.14$ | $25.1 \pm 0.4$ | a |
| [Cr(tn)(aq)₄]³⁺ | $0.650 \pm 0.007$ | $25.9 \pm 0.3$ | a |
| (Cr(chxn)(aq)₄]³⁺ | $6.98 \pm 0.14$ | $27.4 \pm 0.8$ | a |

[a] This work. [b] These results are in agreement with those published earlier for a 3 M perchlorate medium.[2]

*Table 5.* Rate constants at 70 °C and activation energies for the acid hydrolysis of some aminepentaaqua-chromium(III) complexes.

| Complex | $10^6 \, k_1$ (s⁻¹) | $E_A$ (kcal/mol) | Ref. |
|---|---|---|---|
| [Cr(a)(aq)₅]³⁺ | $1.108 \pm 0.011$ | $28.6 \pm 0.2$ | 12 |
| [Cr(enH)(aq)₅]⁴⁺ [b] | $5.4 \pm 0.3$ | $29.0 \pm 1.6$ | a |
| [Cr(tnH)(aq)₅]⁴⁺ | $0.66 \pm 0.02$ | $29.7 \pm 1.0$ | a |
| [Cr(chxnH)(aq)₅]⁴⁺ | $18.5 \pm 1.1$ | $28.8 \pm 1.6$ | a |

[a] This work. [b] See footnote in Table 4.

were therefore carried out. The subsequent calculations were performed assuming the following reactions to occur:

$$[Cr(diam)(aq)_4]^{3+} \underset{k_{12}(obs)}{\overset{k_{21}(obs)}{\rightleftharpoons}} [Cr(diamH)(aq)_5]^{4+}$$

$$\xrightarrow{k_1(obs)} [Cr(aq)_6]^{3+}$$
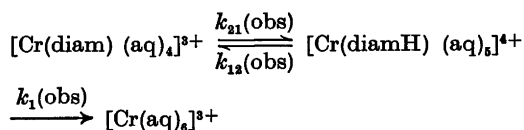
This scheme accurately accommodated the kinetic data, and it was found that the rate constants for the reactions of the (*trans*-2-aminocyclohexylammonium)pentaaquachromium(III) species were dependent on the hydrogen ion concentration, as illustrated in Fig. 4 for the rate constant for the chelation reaction. This latter result points to the kinetic importance of a deprotonated (*trans*-2-aminocyclohexylammonium)pentaaquachromium(III) species.

In order to describe all accumulated data for the different diamine complexes the reaction scheme presented in Fig. 5 must be used. Assuming a constant hydrogen ion concentration the observed rate constants derived from an interpretation of the experimental data within the earlier presented reaction
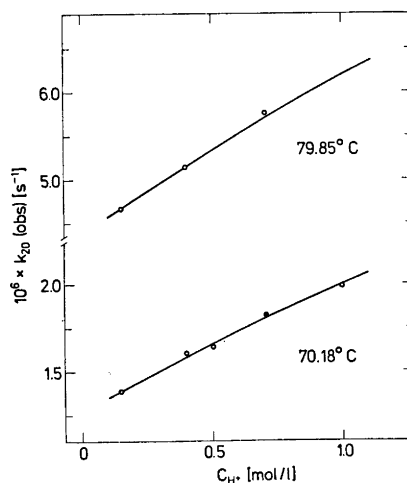


*Fig. 3.* Hydrogen ion concentration dependence of $k_{20}$(obs) for the individual kinetic experiments started with tetraaqua(*trans*-1,2-cyclohexanediamine)chromium(III). Experimental values are indicated by circles and the solid curves are calculated from the rate constants and activation energies in Tables 4, 5 and 6 by means of eqns. 1 and 3. The filled circle indicates the experiment used for Fig. 6.
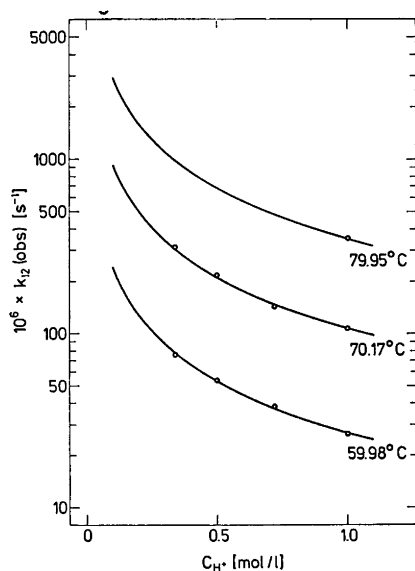
*Fig. 4.* Hydrogen ion concentration dependence of $k_{12}$(obs) for the individual kinetic experiments started with (*trans*-2-aminocyclohexylammonium)pentaaquachromium(III). Experimental values are indicated by circles and the solid curves are calculated from the rate constants and activation energies given in Tables 4, 5 and 6 by means of eqns. 2b and 3.

schemes are related to those of Fig. 5 by the following set of expressions:

$$k_{20}(\text{obs}) = (k_{21}(Kk_1{}^* + k_1[\text{H}^+]))/(Kk_{12} + Kk_1{}^* +$$
$$k_1[\text{H}^+]) \qquad (1)$$

$$k_{21}(\text{obs}) = k_{21} \qquad (2a)$$

$$k_{12}(\text{obs}) = Kk_{12}/(K + [\text{H}^+]) \qquad (2b)$$

$$k_1(\text{obs}) = (Kk_1{}^* + k_1[\text{H}^+])/(K + [\text{H}^+]) \qquad (2c)$$

They are seen to reduce to $k_{21}(\text{obs}) = k_{21}$, $k_{12}(\text{obs}) = 0$ and $k_1(\text{obs}) = k_1$ if $K \ll [\text{H}^+]$ and $Kk_1{}^* \ll k_1$ [H$^+$]. This is in agreement with the experi-

mental results for the hydrolysis of both the 1,2-ethanediamine and 1,3-propanediamine complexes at the acid concentrations employed.

Eqn. (1) was derived assuming a steady state for the concentration of the (*trans*-2-amino-cyclohexylammonium)pentaaquachromium(III) species in experiments started from (*trans*-1,2-cyclohexanediamine)tetraaquachromium(III). This assumption was tested in two different ways. In the first method the hydrogen ion dependence and temperature dependence of observed reaction rate constants were parametrised employing eqns. 1, 2a — 2c and an Arrhenius equation of the form:

$$k_T = k_{T_0} \exp\left[-E_A(1/RT - 1/RT_0)\right] \qquad (3)$$

respectively. Average reaction rate constants at 70 °C and activation energies obtained in this way are tabulated in Tables 4, 5, and 6. These constants, obtained using all the experimental data, have been used for the calculation of the solid curves in Figs. 3 and 4 *via* eqns. 1 and 2b combined with eqn. 3. The calculated curves are seen to adequately describe the observed rate constants obtained for both types of experiment. The values obtained for $k_{21}$(obs) and $k_1$(obs) in the individual kinetic experiments involving the *trans*-1,2-cyclohexanediamine complex were never particularly well-defined. However, reasonably well-defined rate constants and activation energies for hydrolysis of both diamine and monoamine species were obtained in the final calculations. As demonstrated and discussed at greater length previously [•] this again points to the need for independent experiments when complex kinetic schemes are encountered. The second method employed to test the validity of the steady state approximation is demonstrated in Fig. 6, where the excellent agreement between the experimental and calculated
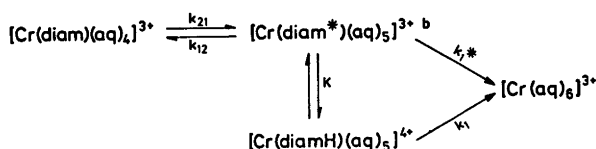


*Fig. 5.* Reaction scheme for acid hydrolysis of diaminetetraaquachromium(III) species. b. Although the species [Cr(diam*) (aq)$_5$]$^{3+}$ is probably the primary hydrolysis product of the [Cr(diam) (aq)$_4$]$^{3+}$ species, differences in acid strength between coordinated water and coordinated protonated amine make it likely that the monoamine species is probably more accurately described by the formula [Cr(diamH) (aq)$_4$OH]$^{3+}$.

*Table 6.* "Rate constants" at 70 °C and "activation energies" for reactions of the deprotonated monoamine species containing monodentate *trans*-1,2-cyclohexanediamine.

| $kK$ | $10^6 \times kK$ [mol/(l × s)] | $E_A$ (kcal/mol) |
|---|---|---|
| $k_{12}K$ [a] | $106 \pm 4$ | $30.8 \pm 0.4$ |
| $k_1{}^*K$ [a] | $22.9 \pm 1.1$ | $36.4 \pm 1.4$ |

[a] With the present data the acidity constant $(K)$ of the (*trans*-2-aminocyclohexylammonium)-pentaaquachromium(III) ion was estimated to be $(2 \pm 2) \times 10^{-2}$ mol/l. A separation of the products $k_{12}K$ and $k_1{}^*K$ into well-defined constants could therefore not be performed.

concentration-time relationship as well as the minor amounts of monoamine species present in solutions confirm the validity of the approximation employed.

The hydrolysis of the tetraaqua((−)$_D$-*trans*-1,2-cyclohexanediamine)chromium(III) ion was also followed by measurement of optical rotation. This method gave rate constants essentially the same as those obtained by spectral monitoring results, but due to relatively large uncertainty in the measured rotations these experiments gave no additional information about the kinetics of the system.

The complete reaction scheme presented here is similar to an earlier proposed scheme for dechelation of both aromatic [10] and aliphatic [11] amines. However, in our system the rate determining step is *not* proton attack on the uncoordinated free amino group, as demonstrated by the successful isolation of the protonated amine intermediate. It may be envisaged that the scheme presented here also applies to some of these other systems since a hydrogen ion dependence of the observed rate constants of the form given by eqn. (1) is observed for both reaction schemes.

In Fig. 7 rate constants for the monoamine complexes investigated are exhibited as a function of the acidity constants for the fully protonated free amines. Although the reactivity differences may be partly rationalized on this basis it can be seen that there is no quantitative correlation.

For the flexible ligands, 1,2-ethanediamine and 1,3-propanediamine, it is likely that different conformations predominate in the diprotonated, the monoprotonated, and the complex-bound monoprotonated forms, and such an effect could explain the deviations from linearity seen in Fig. 7, but further evidence in support of this suggestion is clearly required. Linear correlations have been observed previously for reactions of the type

$$[Cr(aq)_5X]^{(3-i)+} + aq \rightleftharpoons [Cr(aq)_6]^{3+} + X^{i-}$$
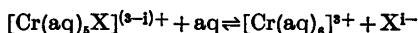
where X is one of a series of anionic ligands (I⁻, Br⁻, Cl⁻, NCS⁻ or F⁻)[13] or one of a series of 3-substituted pyridines.[14] The significant differences in slopes and particularly intercepts for the three correlations are noteworthy, however.
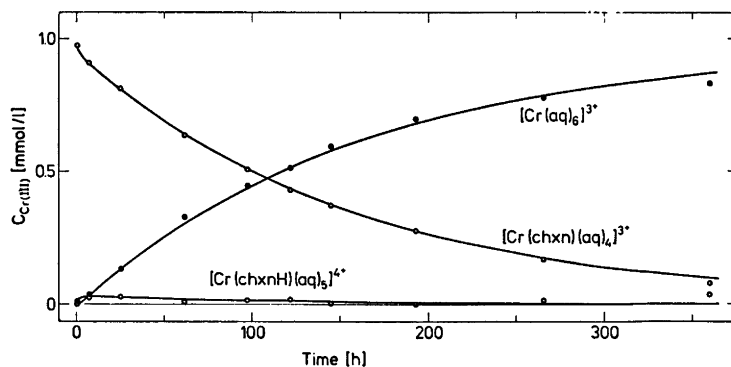


*Fig. 6.* Kinetic experiment started from (*trans*-1,2-cyclohexanediamine) tetraaquachromium(III) (indicated by a filled circle in Fig. 3) interpreted within the reaction scheme of Fig. 5. Circles indicate concentrations calculated from the spectra of reaction mixtures. The solid curves are calculated from rate constants obtained by eqns. 2a, 2b, 2c and 3 from the data given in Tables 4, 5 and 6.
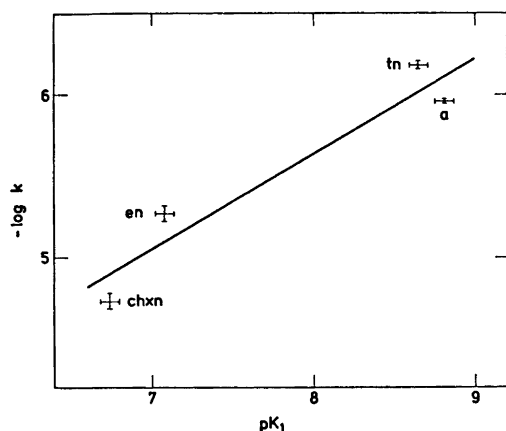
*Fig. 7.* Correlation between $-\log k_1$ and $pK_1$ values at 70 °C, statistically corrected for the number of equivalent ionisable hydrogen atoms in the aminogroups (Tables 5 and 1).

For the protonated polyaminepentaaquachromium(III) complexes of 1,4,7-triazaheptane ("dien"),[15] 1,4,7,10-tetraazadecane ("trien")[16] and 1,4,7,10,13-pentaazatridecane ("tetren")[17] the correlation between hydrolysis rate constants and acidity constants for the fully protonated amines is not good. At 70 °C all the complexes react at a rate comparable to that of the 2-aminoethylammonium complex but the free, fully protonated amines are substantially stronger acids than the diprotonated 1,2-ethanediamine. This absence of correlation is believed to reflect the fact that whereas hydrolysis of the coordinated primary aminogroups is responsible for the observed rate constants, it is the protons on the secondary aminogroups which are mainly responsible for the observed acidity constants.

An approach similar to the one outlined above for the monoamine data is not possible for the diamine data since this would require a knowledge of the acidity constants of the protonated, coordinated diamines in the monoamine complexes. Due to rapid chelation and polymerization reactions these constants are not easily measured. A value for the acidity constant of the (2-aminoethylammonium)pentaaquachromium(III) ion similar to those observed for other chromium(III) complexes of the 2-aminoethylammonium ion ligand [9,18] is, however, capable of rationalizing the reactivity difference between the tetraaqua(1,2-ethanediamine)chromium(III) and cis-diamminetetraaquachromium(III) species on the same basis as discussed for the monoamine complexes. This makes it reasonable to classify the dechelation of 1,2-ethanediamine as a "normal" substitution reaction. For chelate ligands of higher coordination number numerous examples of deviations from such simple behaviour have been found as may be illustrated by comparing the large difference in reactivity between the isomeric triaqua(1,4,7-triazaheptane)chromium(III) ions.[14]

In Table 7 are given equilibrium constants for 1,2-ethanediamine and trans-1,2-cyclohexanediamine as chelate and monodentate protonated ligands. The data show the greater preference of the trans-2-aminocyclohexylammonium ligand than of the 2-aminoethylammonium ligand for forming chelate complexes, but it is not immediately apparent whether the large difference is kinetically determined or is the result of a larger acidity constant for the trans-2-aminocyclohexylammonium complex. The greater importance of the acid dependent monoamine hydrolysis reaction in the case

*Table 7.* Equilibrium constants for 1,2-ethanediamine and trans-1,2-cyclohexanediamine as chelate and protonated monodentate ligands.

| Reaction | $K$ (mol/l) | $t$ (°C) | Ref. |
|---|---|---|---|
| $[Cr(chxnH)(aq)_5]^{4+} \rightleftharpoons [Cr(chxn)(aq)_4]^{3+} + H^+$ | $10^{1.2}$ | 70 | a |
| $[Cr(en)_2(enH)(aq)]^{4+} \rightleftharpoons [Cr(en)_3]^{3+} + H^+$ | $10^{-3.7}$ | 24 | 9 |
| $[Cr(enH)(aq)_5]^{4+} \rightleftharpoons [Cr(en)(aq)_4]^{3+} + H^+$ | $<10^{-1.3}$ [b] | 80 | a |

[a] This work. [b] This value is based upon an upper limit for the rate constant for the chelation reaction of the (2-aminoethylammonium)pentaaquachromium(III) ion, estimated from data for experiment 5 in Table 3.

of the (*trans*-2-aminocyclohexylammonium)-pentaaquachromium(III) ion than in the case of the (2-aminoethylammonium)pentaaquachromium(III) ion could be taken as evidence in favour of the latter explanation. Inspection of molecular models, however, reveals significant interaction between the cyclohexanediamine ring and coordinated water molecules in the (*trans*-2-aminocyclohexylammonium)pentaaquachromium(III) ion. This interaction apparently prevents the uncoordinated amino-group from moving very far away from the first coordination sphere of the complex ion. Such an effect could well result in a larger acidity constant and would at the same time increase the probability of formation of the chelate complex because of the close proximity of the "reactants".

It is clear that further experiments would be of value in throwing more light on many of the points raised in the previous section, and with this in mind an investigation of the hydrolysis of chromium(III) methylamine complexes and of the two isomeric forms of the amminetriaqua(1,2-ethanediamine)-chromium(III) ion is currently in progress.

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