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Acid-base, *cis-trans* and Complex Equilibria in the Chromium(III) Ethylenediamine System

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The three *cis-trans* equilibrium constants and the four acid dissociation constants related to the ions $\mathrm{Cren_2(H_2O)_2^{+++}}$, $\mathrm{Cren_2(OH)(H_2O)^{++}}$ and $\mathrm{Cren_2(OH)_2^{+}}$ have been determined by spectrophotometric and glass electrode measurements, respectively. The absorption spectra of these six ions and of the $\mathrm{Cren_3^{+++}}$ ion have been recorded. In an attempt to determine the stability constant of this last ion its hydrolysis in ethylenediamine buffers at pH ≥ 9.5 has been followed spectrophotometrically. The product of this hydrolysis which proceeds until almost completion except in very concentrated buffers is the *cis-trans* equilibrium mixture of dihydroxobisethylenediaminechromium(III) ions. Only an estimate of the upper limit of the stability constant could be given.

An error in the calculation of the stability constant for the $\mathrm{Coen_3^{+++}}$ ion in Ref.[1] has been corrected (p. 1093).

In the present investigation the acid-base and *cis-trans* equilibria of the following system:

$$\begin{array}{ccccc}
cis\text{-}\mathrm{Cren_2(H_2O)_2^{+++}} & \rightleftharpoons & cis\text{-}\mathrm{Cren_2(H_2O)(OH)^{++} + H^+} & \rightleftharpoons & cis\text{-}\mathrm{Cren_2(OH)_2^{+} + 2H^+} \\
\upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright \\
tr.\text{-}\mathrm{Cren_2(H_2O)_2^{+++}} & \rightleftharpoons & tr.\text{-}\mathrm{Cren_2(H_2O)(OH)^{++} + H^+} & \rightleftharpoons & tr.\text{-}\mathrm{Cren_2(OH)_2^{+} + 2H^+}
\end{array}$$

have been determined and the hydrolysis of $\mathrm{Cren_3^{+++}}$ in acid and alkaline solution has been studied with the intention to determine the complexity constants

$$k_3 = \frac{[\mathrm{Cren_3^{+++}}]}{[\mathrm{Cren_2(H_2O)_2^{+++}}]\ [\mathrm{en}]}$$

for the *cis-* and *trans* ions, respectively.

Further, the spectra between 650 and 325 mμ of all the species mentioned have been recorded.

The measurements have been carried out at 25.0±0.1°C, and in order to eliminate salt effects a comparatively strong constant salt medium of 1 M

$NaNO_3$ has been used. This also renders the quantities calculated directly comparable with those obtained by Bjerrum and Rasmussen [1] for the corresponding Co(III) system.

Following the notation in Ref.[1] * the constants pertaining to the acid-base equilibria are defined as follows:

$$k_{s,1}(cis) = \frac{[H^+]\ [cis\text{-}Cren_2(H_2O)(OH)^{++}]}{[cis\text{-}Cren_2(H_2O)_2{}^{+++}]}$$

$$k_{s,2}(cis) = \frac{[H^+][cis\text{-}Cren_2(OH)_2{}^{+}]}{[cis\text{-}Cren_2(H_2O)(OH)^{++}]}$$

(and the analogous $k_{s,1}(tr.)$ and $k_{s,2}(tr.)$ for the *trans* system), and the *cis-trans* equilibrium constants are defined as follows:

$$q_0 = \frac{[cis\text{-}Cren_2(H_2O)_2{}^{+++}]}{[tr.\text{-}Cren_2(H_2O)_2{}^{+++}]} \quad q_1 = \frac{[cis\text{-}Cren_2(H_2O)(OH)^{++}]}{[tr.\text{-}Cren_2(H_2O)(OH)^{++}]} \quad q_2 = \frac{[cis\text{-}Cren_2(OH)_2{}^{+}]}{[tr.\text{-}Cren_2(OH)_2{}^{+}]}$$

Between these seven constants there are two independent relations, so when five of them are determined experimentally, the remaining two can be calculated.

Preliminary spectrophotometric experiments showed that in acid solution ($1 < pH < 2$) the tris-ethylenediamine ion will hydrolyze to form the *cis*-diaquo ion **, which will in turn hydrolyze forming blue, violet and finally green solutions, while the *trans*-diaquo ion apparently partly will isomerize to form the *cis*-diaquo ion at a rate somewhat higher than that of the hydrolysis.

In alkaline solution, however, it has been possible to establish the *cis-trans* equilibrium and so to determine q_2.

The values of the constants obtained at 25°C and in 1 M $NaNO_3$ are:

$*k_{s,1}(cis) = 10^{-4.80}$ mole/l (Co $10^{-6.06}$) $*k_{s,2}(cis) = 10^{-7.17}$ mole/l (Co $10^{-8.19}$)
$*k_{s,1}(tr.) = 10^{-4.08}$ mole/l (Co $10^{-4.45}$) $*k_{s,4}(tr.) = 10^{-7.49}$ mole/l (Co $10^{-7.94}$)
$q_0 = 12.8$ (Co 58) $q_1 = 2.44$ (Co 1.42) $*q_2 = 5.1$ (Co 0.80)

the quantities marked by an asterisk being calculated directly from measurements upon solutions in which the corresponding equilibria were established.

On comparison with the cobalt system (values from Ref.[1] given in parenthesis) it is seen that the chromium compounds are stronger acids than the corresponding cobalt compounds.

As might be expected empirically [1,3], the *trans*-diaquo ion is a stronger acid than the *cis*-diaquo ion with respect to the dissociation of the first proton, but this difference is smaller than that between the corresponding cobaltic ions. The ratio of the first and second acid dissociation constants is

for the *cis*-diaquo ions $10^{2.37}$ (Co $10^{2.13}$)
" " *trans* " " $10^{3.41}$ (Co $10^{3.39}$)

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* C_A and [A] designate initial and actual concentration of A in mole/liter.

** This is in accordance with the findings of Schläfer and Kling[2], who have made a kinetic investigation of this reaction.

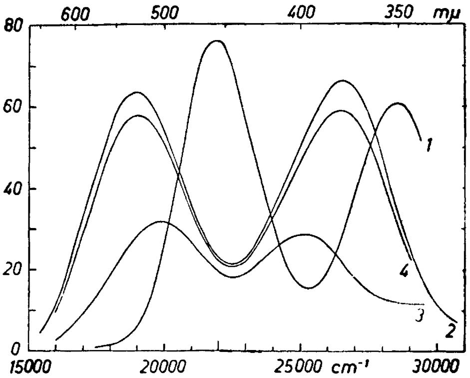

Fig. 1. Spectra in 1 M $NaNO_3$ at 25°C of the ions $Cren_3{+}{+}{+}$ (1), *cis*-$Cren_2(OH)_2{+}$(2) *trans*-$Cren_2(OH)_2{+}$(3) and of the *cis-trans* equilibrium mixture of the $Cren_2(OH)_2{+}$ ions(4). The equilibrium spectrum has been calculated from the spectra of the pure isomers using the *cis-trans* equilibrium constant $q_2 = 5.1$ (see Table 5).
Abscissa: Wave numbers in cm^{-1} and wavelength in mμ.
Ordinate: The molar decadic extinction coefficient.

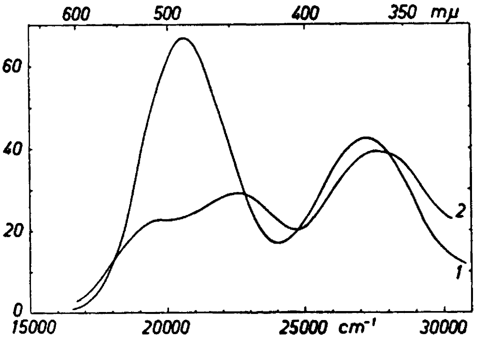

Fig. 2. Spectra in 1 M $NaNO_3$ at 25°C of the ions *cis*-$Cren_2(H_2O)_2{+}{+}{+}$ (1) and *trans*-$Cren_2(H_2O)_2{+}{+}{+}$(2).
Abscissa: Wave numbers in cm^{-1} and wavelength in mμ.
Ordinate: The molar decadic extinction coefficient.

Figs. 1, 2 and 3 show the spectra of the species concerned in this investigation recorded in 1 M $NaNO_3$ solution in the region of 650 mμ—325 mμ, and in Table 1 are given the data of the maxima in the spectra.

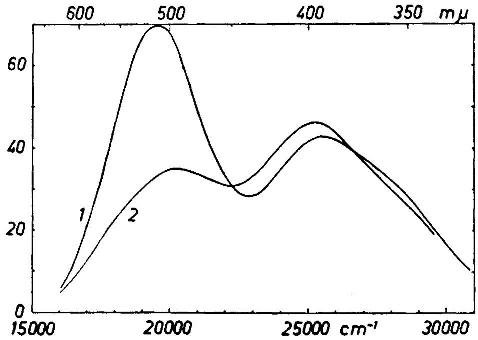

Fig. 3. Spectra in 1 M $NaNO_3$ at 25°C of the ions *cis*-$Cren_2(OH)(H_2O){+}{+}$(1) and *trans*-$Cren_2(OH)(H_2O){+}{+}$(2). These spectra are the averages of those calculated from the solutions in Table 2 which differed 2—3 % with respect to the extinction coefficients.
Abscissa: Wave numbers in cm^{-1} and wavelength in mμ.
Ordinate: The molar decadic extinction coefficient.

Table 1. Data of maxima in the spectra shown in Figs. 1, 2 and 3; 25°C, 1 M $NaNO_3$.

Ion	1. maximum cm^{-1}	 ε	2. maximum cm^{-1}	 ε	3. maximum cm^{-1}	 ε
$\mathrm{Cren_3^{+++}}$	21 880	76.5	28 500	60.7		
cis-$\mathrm{Cren_2(H_2O)_2^{+++}}$	20 650	67.0	27 250	42.5		
tr.-$\mathrm{Cren_2(H_2O)_2^{+++}}$	19 700	22.5	22 600	29.3	27 700	39.2
cis-$\mathrm{Cren_2(OH)(H_2O)^{++}}$	19 550	69.3	25 550	43.0		
tr.-$\mathrm{Cren_2(OH)(H_2O)^{++}}$	20 200	35.0	25 250	46.0		
cis-$\mathrm{Cren_2(OH)_2^{+}}$	19 000	63.6	26 550	66.0		
tr.-$\mathrm{Cren_2(OH)_2^{+}}$	19 900	31.8	25 250	28.9		

The absorption curves have been measured at 25° ± 1°C by means of a Cary Recording Spectrophotometer.

The $\mathrm{Cren_3^{+++}}$ ion is sufficiently robust for a direct recording of its spectrum in acid, neutral and alkaline solutions. As expected the spectra thus obtained are identical and in fair agreement with spectra published earlier [2,4].

The *cis*- and *trans*-$\mathrm{Cren_2(H_2O)_2^{+++}}$ and $\mathrm{Cren_2(OH)_2^{+}}$ ions, however, are so labile that small changes in the absorption of their solutions can be registered within a few minutes after preparation of the solutions. Therefore the following procedure was used in recording their spectra: The solvent was prepared at 25°C, the solute added and dissolved at time 0 and the solution made up to the mark and the first absorption curve recorded at time 3 min. During the next 15 min another 3 absorption curves were recorded on the same sheet, and the absorption curve of the pure substance was then obtained by extrapolation to time 0. In all cases the differences between the curve obtained after 3 min and the extrapolated curve were very small, namely from 1 to 3 times the experimental uncertainty. In each case the pH of the solution was measured immediately after preparation.

The spectra of the *cis*- and *trans*-aquohydroxo ions have been calculated from the absorption curves of solutions, the pH of which has been adjusted so that they would contain a relatively large concentration of the ion in question, a smaller concentration of either the corresponding diaquo or dihydroxo ion and a negligible amount of the remaining of these three ions. The data of these solutions are given in Table 2.

A calculation of the spectrum of the *cis*-$\mathrm{Cren_2(OH)(H_2O)^{++}}$ from the two first solutions by subtracting the absorption of the $\mathrm{Cren_2(H_2O)_2^{+++}}$ and the $\mathrm{Cren_2(OH)_2^{+}}$, respectively, from the total absorption of the solutions yielded

Table 2. Composition of the solutions from which the spectra of the *cis*- and *trans*-$\mathrm{Cren_2(OH)(H_2O)^{++}}$ have been calculated. C_{Cr} indicates total complex concentration. Concentrations are in mole/l. 25°C, 1 M $NaNO_3$.

C_{Cr}	pH	$[\mathrm{Cren_2(OH)(H_2O)^{++}}]$	$[\mathrm{Cren_2(OH)_2^{+}}]$	$[\mathrm{Cren_2(H_2O)_2^{+++}}]$
0.02875 *cis*	5.033	0.0181	0.0002	0.0105
0.02879 *cis*	6.517	0.0235	0.0052	0.0001
0.01268 *tr.*	5.876	0.0122	0.0003	0.0002
0.00973 *tr.*	4.159	0.00532	negligible	0.00441

two curves which were in complete agreement with respect to the wavelengths of their maxima and differed less than 2 % with respect to the extinction coefficients. Similar results were obtained for the *trans*-$Cren_2(OH)(H_2O)^{++}$ except that the difference between the extinction coefficients at some wavelengths amounted to as much as 3 %. This agreement furnishes a good cross-check of the values of the acid dissociation constants.

An interesting feature of these two spectra is the "shoulder" near 29 000 cm^{-1} which at least in the *cis*-spectrum seems far beyond the experimental uncertainty.

EXPERIMENTAL

Preparations. $Cren_3Cl_3,3\frac{1}{2}H_2O$ was prepared from $CrCl_3$ and anhydrous ethylenediamine according to the method of Linhard and Weigel [5] except that the precipitation was effected by means of ethanol instead of NH_4Cl. (It was found by analysis that precipitates produced by NH_4Cl contained NH_4Cl which was difficult to remove by recrystallization.) The salt was reprecipitated and the spectrum was shown not to be influenced by further reprecipitations or recrystallizations.

cis- and trans-$Cren_2(H_2O)_2Br_3$ were prepared according to the following scheme:

$$\begin{tikzcd}
Cren_3(ClO_4)_3 \arrow[r, "HCl"', "70^\circ"] & cis\text{-}Cren_2Cl_2ClO_4 \arrow[r] \arrow[d, "HgBr_2"', "HBr"] & cis\text{-}Cren_2(OH)(H_2O)S_2O_6 \arrow[r] & cis\text{-}Cren_2(H_2O)_2Br_3,2H_2O \\
& tr.\text{-}(Cren_2Br_2)Br,HgBr_2 \arrow[r] & tr.\text{-}Cren_2(OH)(H_2O)Br_2 \arrow[r] & tr\text{-}Cren_2(H_2O)_2Br_3,2H_2O
\end{tikzcd}$$

cis-$Cren_2Cl_2ClO_4$ was prepared according to Ref.[5], p. 119. To prepare *cis*-$Cren_2(H_2O)_2Br_3$, 6 g *cis*-$Cren_2Cl_2ClO_4$ was dissolved in *ca.* 50 ml warm water and the solution heated until colour change from violet to orange. 10 ml pyridine and excess of $Na_2S_2O_6$ were added and the solution cooled in ice for 1 h whereby the *cis*-aquohydroxo dithionate was precipitated. Treament of this with HBr yielded *ca.* 3 g *cis*-$Cren_2(H_2O)_2Br_3$, $2H_2O$.

To prepare the corresponding *trans*-compound 8.5 g *cis*-$Cren_2Cl_2ClO_4$ was dissolved in 30 ml water at 50°C and 16 g $HgBr_2$ and 16 ml const. boil. HBr were added. The solution was evaporated to dryness on the steam bath and the residue washed with water containing HBr until colourless filtrate, leaving bright green, slightly soluble crystals of *trans*-$(Cren_2Br_2)Br,HgBr_2$ in a yield of 13.5 g. A suspension of 19 g of this salt in 20 ml water was saturated with H_2S and the HgS removed by centrifuging. Spectra of the solution recorded at regular intervals indicated that a maximum of *trans*-$Cren_2(H_2O)_2^{+++}$ was present after 24–36 h at *ca.* 22°C. The solution was then saturated with KBr and 20 ml pyridine was added. The pink precipitate formed after cooling in ice for 1 h was washed several times with 50 % ethanol to remove most of a considerable content of KBr, leaving 2.5 g *trans*-$Cren_2(H_2O)(OH)Br_2$. Treatment of this salt with the equivalent amount of const. boil. HBr yielded 2.2 g *trans*-$Cren_2(H_2O)_2Br_3,H_2O$.

The diaquobisethylenediamine salts were originally prepared by Pfeiffer [6] along the path outlined here

$$CrCl_2(H_2O)_4Cl,2H_2O \xrightarrow{py} Crpy_2(OH)_2(H_2O)_2Cl \xrightarrow{en} (Cren_2(H_2O)Br)Br_2$$

$$\begin{tikzcd}
(Cren_2(H_2O)Br)Br_2 \arrow[r] \arrow[d, "HgBr_2"', "HBr"] & cis\text{-}Cren_2(OH)(H_2O)Br_2 \arrow[r] & cis\text{-}Cren_2(H_2O)_2Br_3,2H_2O \\
tr.\text{-}(Cren_2Br_2)Br,HgBr_2 \arrow[r] & tr.\text{-}Cren_2(OH)(H_2O)Br_2 \arrow[r] & tr.\text{-}Cren_2(H_2O)_2Br_3,H_2O
\end{tikzcd}$$

Considering that $Cren_3Cl_3$ is now so easily accessible, the procedure outlined above seems more convenient.

Analysis. The salts prepared have been analyzed as follows. *Chromium* has been determined on a semimicro scale either by decomposition with sulfuric acid, heating in

Table 3. Analysis.

Formula and formula weight	Equiv. weight based on Cr	Equiv. weight based on halogen	Equiv. weight based on N	Equiv. weight as an acid
$Cren_3Cl_3,3\frac{1}{2}H_2O$ 401.8	calc. 401.8 found 400.0 (titr.)	calc. 133.9 found 132.6	calc. 66.97 found 67.30	
cis-$Cren_2(H_2O)_2Br_3,2H_2O$ 484.1	calc. 484.1 found 481.3 (titr.)	calc. 161.4 found 161.3		calc. 242.0 found 242.3
tr.-$Cren_2(H_2O)_2Br_3,H_2O$ 466.0	calc. 466.0 found 464.4 (Cr_2O_3)	calc. 155.3 found 155.6		calc. 233.0 found 233.8

hydrogen atmosphere and weighing as Cr_2O_3, or by a complexometric method, boiling the salt with a known amount of ethylenediaminetetraacetic acid in a buffer solution at pH about 4.6 and back titrating the excess of ENTA with zinc sulfate, using eriochromschwartz as an indicator[2].

Halogen has been determined by weighing as silver halide and *nitrogen* by the Kjeldahl method.

The diaquo salts have been titrated potentiometrically as dibasic acids.

The results of these analyses are given in Table 3.

ACID DISSOCIATION CONSTANTS OF THE DIAQUO- AND THE AQUOHYDROXO-IONS

The acid dissociation constants of the *cis-* and *trans*-diaquobisethylenediamine ions at 25°C were calculated from glass electrode measurements of hydrogen ion concentrations in solutions of the complex salts partly neutralized with sodium hydroxide.

The measurements were made with a selected glass-electrode the performance of which had been tested[7] and a PHM 3 pH-meter from "Radiometer", Copenhagen.

Readings of the EMF of the cell glass-electrode calomel electrode are designated E.

As a standard was used dilute nitric acid in which $C_{HNO_3} = 0.005005$; $C_{NaNO_3} = 1.000$. Readings in this solution are designated E_{st}.

As a consequence of the isomerization of the *cis-* and *trans*-ions and the difference in acid strength of the corresponding *cis-* and *trans*-acids, the hydrogen ion concentration in a (freshly prepared) solution of a pure *cis-* or *trans*-salt will vary with time.

By a rapid preparation of the solutions it was possible to make the first measurement 30 sec after the solid had dissolved * (when finely powdered, the salts dissolve very rapidly). The measurements were then continued for

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* The glass-electrode requires some time for its adjustment, so meaningful measurements can hardly be made faster.

some time and E was recorded as a function of time. The E data of Table 4 are the results of an extrapolation of these functions to time zero. The rate of change of E was in no case higher than 1.5 mV/min. E_{st} was recorded before and after each set of measurements, and the results never varied more than 0.3 mV.

The acid dissociation constants have been calculated by means of formulae of the type derived by J. Bjerrum [1,8].

The average number of protons produced by the diaquo ion may be calculated from the experimental quantities as

$$\bar{\nu} = \frac{C_{\mathrm{NaOH}} + [\mathrm{H}^+] - [\mathrm{OH}^-]}{C_{\mathrm{Cr}}}$$

and expressed in terms of $k_{s,1}$ and $k_{s,2}$ as

$$\bar{\nu} = \frac{k_{s,1}[\mathrm{H}^+] + 2k_{s,2}\cdot k_{s,2}}{[\mathrm{H}^+]^2 + k_{s,1}[\mathrm{H}^+] + k_{s,1}\cdot k_{s,2}}$$

Combining these expressions and rearranging, one obtains for $\nu < 1$

$$-\log k_{s,1} = -\log[\mathrm{H}^+] + \log\frac{1-\bar{\nu}}{\bar{\nu}} + \log\left(1 + \frac{(2-\bar{\nu})k_{s,2}}{(1-\bar{\nu})\,[\mathrm{H}^+]}\right)$$

for $\bar{\nu} > 1$

$$-\log k_{s,2} = -\log\,[\mathrm{H}^+] + \log\frac{2-\bar{\nu}}{1-\bar{\nu}} - \log\left(1 + \frac{\bar{\nu}[\mathrm{H}^+]}{(\bar{\nu}-1)k_{s,1}}\right)$$

In the experiments recorded in Table 4 $\bar{\nu}$ has been kept close to 0.5 and 1.5, respectively, in order to ensure the smallest possible uncertainty in the calculated constants (*i.e.* in the terms $\frac{1-\bar{\nu}}{\bar{\nu}}$ and $\frac{2-\bar{\nu}}{\bar{\nu}-1}$, respectively).

THE *cis-trans* EQUILIBRIUM CONSTANTS

Spectrophotometric experiments have shown that in acid solution the *trans*-$\mathrm{Cren_2(H_2O)_2^{+++}}$ isomerizes to form the corresponding *cis*-ion (roughly estimated the conversion is almost completed within 24 h at 25°C in 1 M $\mathrm{NaNO_3}$, $[\mathrm{H}^+] \sim 0.02$). But the rate of hydrolysis of the *cis*- and the *trans*-ions can not be neglected in comparison to the rate of isomerization. Thus the spectrum of a 24 h old solution of the *cis*-salt cannot be very accurately represented by a linear combination of the spectra of the *cis*- and *trans*-ions. Because of this hydrolysis and because of the fact that the equilibrium mixture of the two ions according to a rough calculation would contain less than 10 % of the *trans*-ion, no attempt has been made to determine the *cis-trans* equilibrium constant in acid solution.

In an ethylenediamine buffer solution at about pH = 10 the *cis*- and *trans*-$\mathrm{Cren_2(OH)_2^+}$ are sufficiently stable to allow the *cis-trans* equilibrium to be established. Such equilibrium mixtures have been analyzed spectrophotometrically and chromatographically.

Table 4. The acid dissociation constants of the diaquobisethylenediaminechromium(III) ions in 1 M sodium nitrate at 25°C.

$C_{NaNO_3} = 1.000$ $-\log[H^+]_{st} = 2.3006$

The first dissociation constant $\Delta = \frac{(2-\bar{\nu})k_{s,2}}{(1-\bar{\nu})[H^+]}$

No.	$C_{Cr}(cis)$	C_{NaOH}	$\bar{\nu}$	$E_{st}-E$	$-\log[H^+]$	$\log\frac{1-\bar{\nu}}{\bar{\nu}}$	$\log(1+\Delta)$	$-\log k_{s,1}$
1	0.009841	0.005094	0.5191	0.1505	4.8471	−0.0331	0.0055	4.820
2	0.01058	0.005106	0.4843	0.1454	4.7608	0.02731	0.0045	4.793
3	0.01606	0.005094	0.3194	0.1273	4.4546	0.3286	0.0019	4.785
						Av. $-\log k_{s,1}$ (*cis*):		4.80
	$C_{Cr}(tr.)$							
4	0.01726	0.01562	0.9054	0.1624	5.0485	−0.9811	0.0183	4.086
5	0.01046	0.005106	0.4965	0.1039	4.0586	0.0061	0.0005	4.065
6	0.01068	0.005106	0.4865	0.1035	4.0519	0.0234	0.0005	4.076
						Av. $-\log k_{s,1}$ (*tr.*):		4.08

The second dissociation constant $\Delta = \frac{\bar{\nu}[H^+]}{(\bar{\nu}-1)k_{s,1}}$

No.	$C_{Cr}(cis)$	C_{NaOH}	$\bar{\nu}$	$E_{st}-E$	$-\log[H^+]$	$\log\frac{2-\bar{\nu}}{\bar{\nu}-1}$	$-\log(1+\Delta)$	$-\log k_{s,2}$
7	0.01057	0.01566	1.4815	0.2862	7.1432	0.0321	0.0059	7.169
8	0.01016	0.01562	1.5372	0.2914	7.2312	−0.0647	0.0045	7.162
9	0.008397	0.01566	1.8645	0.3355	7.9774	−0.8049	0.0006	7.172
						Av. $-\log k_{s,2}$ (*cis*):		7.17
	C_{Cr}(tr.)							
10	0.01145	0.01566	1.3675	0.2926	7.2515	0.2357	−0.0011	7.485
11	0.009407	0.01562	1.6603	0.3231	7.7676	−0.2886	−0.0002	7.479
12	0.009065	0.01566	1.7272	0.3331	7.9368	−0.4259	−0.0001	7.511
						Av. $-\log k_{s,2}$ (*tr.*):		7.49

For the spectrophotometric determination of the *cis-trans* constant a weighed amount of *cis-* (or *trans-*) $Cren_2(H_2O)_2Br_3,2H_2O$ was dissolved in a suitable ethylene diamine buffer solution prepared from standard ethylene diamine solution, standard nitric acid and 5 M $NaNO_3$ in such a way that in the final solution pH would be close to 10 and $[NO_3^-] = 1$.

The solution was prepared and kept at 25°C in a dark bottle, and the spectrum of the solution was recorded immediately after preparation and at intervals until no further change could be observed. The *cis-* as well as the *trans*-solutions finally exhibited the equilibrium spectrum shown in Fig. 1 corresponding to 83.6 % *cis-* and 16.4 % *trans*-$Cren_2(OH)_2^+$.

Table 5 shows the data from four experiments of this type from which q_2 may be calculated. ε_{cis} and $\varepsilon_{tr.}$ designate the extinction coefficients of *cis-* and *trans*-$Cren_2(OH)_2^+$, respectively. The quantities $\varepsilon_{cis} - \varepsilon_t$ and $\varepsilon_t - \varepsilon_{tr.}$ have been calculated from the spectra using the formula $\frac{|D^\circ - D^t|}{l \times C_{Cr}}$ where

$|D^\circ - D^t|$ is the difference in the optical density of the solution at time 0 and at time t read directly from the curves recorded by the Cary, and l is the cell length. The degree of reaction, α, α has been calculated from $\alpha = \frac{\varepsilon_{cis} - \varepsilon_t}{\varepsilon_{cis} - \varepsilon_{tr.}}$ and $\alpha = \frac{\varepsilon_t - \varepsilon_{tr.}}{\varepsilon_{cis} - \varepsilon_{tr.}}$ and q_2 from $q_2 = \frac{1-\alpha}{\alpha}$, and $q_2 = \frac{\alpha}{1-\alpha}$, respectively.

In order to check these values further, an aliquot of each of the equilibrium solutions was acidified by means of nitric acid, the volume was doubled after addition of sufficient $NaNO_3$ to keep $[NO_3^-] = 1$, and the spectrum was recorded immediately after. When working fast, one may assume that the ratio of the *cis*- and *trans*-ions will remain almost unchanged during this procedure, so q_2 may likewise be calculated from these spectra. The results of these experiments are also given in Table 5. Here ε_{cis} and $\varepsilon_{tr.}$ designate the extinction coefficients of *cis*- and *trans*- $Cren_2(H_2O)_2^{+++}$, respectively.

For the chromatographic determination of the *cis-trans* constant was used a two years old solution prepared by dissolving $Cren_3Cl_3$ in an ethylenediamine buffer of a composition similar to that mentioned above *. As will be seen from the following, the $Cren_3^{+++}$ in such a solution will be converted into an equilibrium mixture of *cis*- and *trans*-$Cren_2(OH)_2^+$ whereupon a very slow process of unknown character takes place. Due to practical difficulties the solution could not be kept at 25 + 0.1°C for two years but prior to the following experiment it was kept at 25°C for some days in order to establish the equilibrium between possible contents of *cis*- and *trans*-$Cren_2(OH)_2^+$ corresponding to this temperature.

By a technique similar to that described in Ref.[9] an aliquot of the solution was then chromatographed on a column of Al_2O_3. The eluate obtained using 0.1 M KOH, 1 M KCl as an eluent, contained two red fractions which were collected separately in nitric acid at 0° and examined spectrophotometrically. The shape of the spectra (*i.e.* number and position of bands and the relative heights of these bands) was identical with the shape of the spectra of *trans*- and *cis*-$Cren_2(H_2O)_2^{+++}$, respectively, the first of the fractions exhibiting the *trans* spectrum.

Experiments showed that when a freshly prepared solution of *cis*- and *trans*-$Cren_2(OH)_2^+$ is run through the column, the two ions get separated and may be collected at a loss of only a few per cent of each. In accordance with a rule that seems rather general the *trans* ion shows the weaker adsorption on the column.

This strongly indicates that the two red fractions from the equilibrium solution actually represent its content of *trans*- and *cis*-$Cren_2(OH)_2^+$.

Since the eluate from the column was too dilute to permit an accurate spectrophotometric determination of the content of *cis*- and *trans*-$Cren_2(H_2O)_2^{+++}$, the chromium content in the two fractions was instead determined titrimetrically. (Decomposition by evaporating to dryness, heating the residue with H_2SO_4, dissolving and oxidizing chromium(III) to chromium(VI) by means of $K_2S_2O_8$ in the presence of Ag^+, and finally titrating with Fe^{++} using barium diphenylaminesulfonate as an indicator [10].)

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* solution No. 2 in Table 7.

*Table 5. cis-trans*Equilibrium of the dihydroxobisethylenediaminechromium(III) ions in *ca.* 1 M $NaNO_3$ at 25°C.

Initial composition of solutions.

No.	Cr salt	$C_{Cr}(cis)$	C_{en}	C_{HNO_3}	C_{NaNO_3}	$-\log[H^+]$
1	*cis*-$Cren_2(H_2O)_2Br_3$, $2H_2O$	0.00920	0.0978	0.0463	0.900	9.90
2	—»—	0.00884	0.1413	0.0463	0.900	10.30
		$C_{Cr}(tr.)$				
3	*tr.*-$Cren_2(H_2O)_2Br_3$, H_2O	0.00810	0.0978	0.0463	0.900	9.95
4	—»—	0.01148	0.1413	0.0463	0.900	10.30

Extinction coefficients measured in alkaline solution.

No.	λ	*t* h	375	400	500	525 mμ	Av.
	ε_{cis}		65.7	50.1	54.2	63.4	
	$\varepsilon_{tr.}$		20.3	28.7	31.6	28.5	
	$\varepsilon_{cis} - \varepsilon_{tr.}$		45.4	21.4	22.6	24.9	
1	$\varepsilon_{cis} - \varepsilon_t$	216 (const. for 3 months)	9.2	4.5	4.2	6.3	
	α		20.3 %	21.0 %	18.6 %	18.0 %	19.5 %
	q_2						4.13
2	$\varepsilon_{cis} - \varepsilon_t$	168 (const. for 2 months)	6.2	2.8	3.0	4.5	
	α		13.7 %	13.1 %	13.3 %	12.9 %	13.3 %
	q_2						6.52
3	$\varepsilon_t - \varepsilon_{tr,}$	21	21.0	9.9	9.9	16.7	
	α		46.3 %	46.4 %	43.8 %	47.8 %	46.1 %
	$\varepsilon_t - \varepsilon_{tr.}$	70 (const. for 2 months)	37.2	17.6	18.1	28.3	
	α		81.4 %	82.2 %	80.1 %	81.1 %	81.2 %
	q_2						4.32
4	$\varepsilon_t - \varepsilon_{tr.}$	27 h	20.7	10.1	9.6	15.0	
	α	27 h	45.6 %	47.2 %	42.5 %	43.0 %	44.6 %
	$\varepsilon_t - \varepsilon_{tr.}$	72 (const. for 2 weeks)	38.4	18.0	19.4	28.3	
	α		84.5 %	84.0 %	85.8 %	81.1 %	83.9 %
	q_2						5.21
			Average of q_2 for soln. No. 1—4:				5.1

Extinction coefficients measured immediately after acidifying.

No.	λ	*t* days	487.5	500 mμ	Av.	Av.
	ε_{cis}		66.3	61.0		
	$\varepsilon_{tr.}$		22.9	22.5		
	$\varepsilon_{cis} - \varepsilon_{tr.}$		43.4	38.5		
1	$\varepsilon_{cis} - \varepsilon_t$	99	9.6	6.7		
	α		22.1 %	17.4 %	19.8 %	
	q_2					4.05
2	$\varepsilon_{cis} - \varepsilon_t$	14	6.3	5.5		
	α		14.7 %	14.3 %	14.5 %	
	q_2					5.90
3	$\varepsilon_t - \varepsilon_{tr.}$	65	35.1	31.8		
	α		80.9 %	82.6 %	81.7 %	
	q_2					4.46
4	$\varepsilon_t - \varepsilon_{tr.}$	14	37.2	32.8		
	α		85.6 %	85.2 %	85.4 %	
	q_2					5.84
			Average of q_2 for soln. No. 1—4:			5.1

The eluate from a chromatogram of 20 ml equilibrium solution was found to contain: in the *trans* fraction 0.029 mmole and in the *cis* fraction 0.133 mmole chromium. (This corresponds to about 60 % of the original chromium content of the solution. The rest of the chromium was so strongly adsorbed on the column that it could not be displaced.) Thus $q_2 = 4.6$ with an estimated uncertainty of ± 10 %.

However, the spectrophotometric determinations of q_2 given in Table 5 must be considered the more accurate, and the average of these $q_2 = 5.1$ combined with $k_{s,1}(cis)$, $k_{s,2}(cis)$, $k_{s,1}(tr.)$ and $k_{s,2}(tr.)$ yields $q_1 = 2.44$ and $q_0 = 12.8$.

THE HYDROLYSIS OF THE TRISETHYLENEDIAMINECHROMIUM(III) ION IN ALKALINE SOLUTION

In order to determine the complexity constants

$$k_3 = \frac{[\mathrm{Cren_3}]}{[\mathrm{Cren_2(H_2O)_2}^{+++}][\mathrm{en}]}$$

(for the *cis*- and *trans*-ions, respectively) it was attempted to establish the equilibrium

$$\mathrm{Cren_3}^{+++} + 2\ \mathrm{OH}^- \rightleftharpoons \mathrm{Cren_2(OH)_2}^+ + \mathrm{en}$$

at 25°C in a 1 M salt medium. Preliminary spectrophotometric experiments have shown that in a strongly alkaline (as well as in acid) solution the hydrolysis will proceed further than this first step. On the other hand, test tube experiments have shown that a solution of $\mathrm{Cren_3Cl_3}$ in the following medium: 2 g en,2HCl + 2 g 75 % en + 3 ml H_2O ($\mathrm{enH^+/en} \sim 3$) will stay yellow at room temperature as well as at 100°C. And a solution of $\mathrm{Cren_2(H_2O)_2Br_3}$ in this medium slowly turns yellow. Therefore it was hoped that the above equilibrium could be established in an ethylenediamine buffer at about pH = 10 ($pk_{\mathrm{enH}^+} = 10.2$, Ref. [11]).

In such solutions it would be possible to follow the hydrolysis and to calculate $[\mathrm{Cren_3}^{+++}]$ and $[\mathrm{Cren_2(OH)_2}^+]$ in an eventual equilibrium solution spectrophotometrically, and [en] could be determined by means of glass-electrode measurements. Provided that the above hydrolysis is the only reaction taking place, the degree of conversion of $\mathrm{Cren_3}^{+++}$ into $\mathrm{Cren_2(OH)_2}^+$, α, in a solution in which the initial concentration of $\mathrm{Cren_3}^{+++}$ is C_{Cr}, may be calculated from

$$\alpha = \frac{D_0 - D_\alpha}{l \times C_{\mathrm{Cr}}(\varepsilon_{\mathrm{Cren_3}^{+++}} - \varepsilon_{\mathrm{Cren_2(OH)_2}^+})} \tag{1}$$

where D_0 and D_α are the optical densities at the wavelength λ of the solution before and after the conversion has taken place, while ε is the extinction coefficient at the wavelength λ of the species in the subscript, and l is the cell length.

Table 6. Data of isosbestic points. The uncertainties refer to the reproducibility of the isosbestic points.

Composition of solution	$Cren_3^{+++}$ *cis*-$Cren_2(OH)_2^+$	$Cren_3^{+++}$ *cis-trans* equilibrium mixture of $Cren_2(OH)_2^+$	No. 1 Table 7	No. 2 Table 7
Isosbestic points	Calculated from spectra in Fig. 1		Observed	
mμ	360.7	362.3	362.2 ± 1.0	362.5 ± 0.5
	418.3	417.5	417.0 ± 0.5	417.0 ± 0.5
	487.8	489.0	488.5 ± 0.5	488.8 ± 0.5
ε	53.9	50.2	49.7 ± 0.5	50.5 ± 0.5
	33.3	32.3	32.0 ± 0.5	33.3 ± 0.5
	44.5	43.0	44.0 ± 0.5	42.8 ± 0.5

Calculating α in an equilibrium solution, one should obviously insert for $\varepsilon_{Cren_2(OH)_2^+}$ the extinction coefficient of the *cis-trans* equilibrium mixture of the dihydroxo ions *. When calculating α in a solution not yet in equilibrium, one is presented with the question of which value to insert for $\varepsilon_{Cren_2(OH)_2^+}$. It seems reasonable to assume that the first hydrolysis product would be the *cis*-dihydroxo ion which would then isomerize to form the *cis-trans* equilibrium mixture:

$$Cren_3^{+++} \rightarrow cis\text{-}Cren_2(OH)_2^+ \rightleftharpoons tr.\text{-}Cren_2(OH)_2^+$$

Qualitatively it may be seen that if the isomerization were fast compared to the hydrolysis, it would be permissible to consider the ratio

$$\frac{[tr.\text{-}Cren_2(OH)_2^+]}{[cis\text{-}Cren_2(OH)_2^+]}$$

as a constant (and equal to the equilibrium ratio) during the reaction; otherwise this ratio would be a function of time increasing from zero to the equilibrium ratio.

This problem might be circumvented by choosing values of λ within a range where there is very little difference between the extinction of the *cis* ions and the extinction of the *cis-trans* equilibrium mixture (*vide* Fig. 1).

But fortunately the question may be settled spectrophotometrically by consideration of the isosbestic points which are likewise useful in deciding whether $Cren_3^{+++}$ and *cis*- and *trans*-$Cren_2(OH)_2^+$ are the only species present in the solutions.

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* provided concentrations of *cis*- and *trans*-$Cren_2(OH)(H_2O)^{++}$ may be neglected. For the purpose of the following discussion this approximation is certainly sufficient for pH > 9.5. Due to the similarity between the spectra of the ions in question the correction that would have to be made for the content of $Cren_2(OH)(H_2O)^{++}$ does not exceed the experimental uncertainty until this content exceeds 5 % of $[Cren_2(OH)_2^+]$.

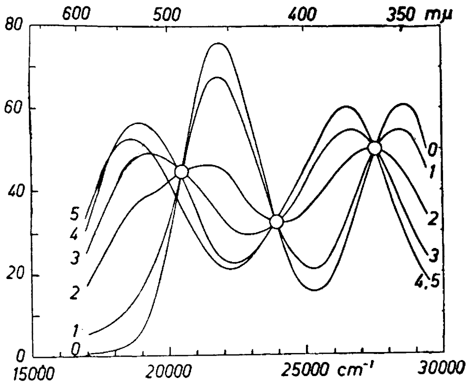

Fig. 4. Spectra in 1 M $NaNO_3$ at 25°C of solution No. 1 in Table 7 at time 0 (0), 69 h (1), 334 h (2), 624 h (3), 1 800 h (4) and 5 900 h (5).
Abscissa: Wave numbers in cm^{-1} and wavelength in mμ.
Ordinate: The molar decadic extinction coefficient.

A number of solutions of $Cren_3Cl_3$ in ethylenediamine buffers at pH $\geqq$ 9 containing the buffer system in various concentrations has been prepared and followed spectrophotometrically and by glass electrode measurements. In no cases, however, it was possible to establish an equilibrium containing analyzable amounts of $Cren_3^{+++}$.

To illustrate the results of these experiments the data of two representative solutions are given in Table 7 and the spectra of No. 1 of these are recorded in Fig. 4. It is seen that all of the consecutive spectra (except that at t=5 900 h) have three common points of intersection. In Table 6 the wavelengths at which these points occur are compared to those which may be predicted from the spectra in Fig. 1 assuming that the components of the mixture are either $Cren_3^{+++}$ and *cis*-$Cren_2(OH)_2^+$ or $Cren_3^{+++}$ and the *cis-trans* equilibrium mixture of the dihydroxo ions. Further the isosbestic extinction coefficients observed ($\varepsilon = D/C_{Cr} \times$ cell length) are compared to those calculated under the two assumptions. A fairly good agreement is found with the assumption that the *cis-* and *trans*-dihydroxo ions are present in their equilibrium ratio. But the points of intersection in the spectra of the reaction mixtures can of course not be determined very accurately until the shape of the spectrum is considerably different from the initial shape. The validity of the above arguments is therefore limited to solutions in which α > *ca.* 40 %, although there is no experimental evidence against their validity at lower values of α*.

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* This agreement is, therefore, not at variance with the assumption that the *cis*-dihydroxo ion is the first hydrolysis product. If one solves the differential equations pertaining to the mechanism

$$A \xrightarrow{k_1} B \underset{k_3}{\overset{k_2}{\rightleftharpoons}} C$$

and calculates the ratio [B]/[C] as a function of time in a system which at time zero contains only A inserting $k_3 = 5k_2 = 10k_1$ (which is not very far from correct for the solutions considered here, vide Tables 5 and 7), one finds that when 50 % of A has disappeared [B]/[C] is only 12 % greater than the equilibrium value.

Table 7. The hydrolysis of the trisethylenediaminechromium(III) ion in ethylenediamine buffers at pH ~10 in *ca.* 1 M nitrate at 25°C.

Data of initial solutions. $-\log[H^+]_{st} = 2.3006$

No.	Cr salt	C_{Cr}	C_{en}	C_{HNO_3}	C_{NaNO_3}	$E_{st}-E$	$-\log[H^+]$
1	$Cren_3Cl_3$, $3\frac{1}{2}H_2O$	0.01235	0.09806	0.06545	0.9000	0.4436	9.807
2	—»—	0.01371	0.4903	0.3200	0.6700	0.4523	9.954

Spectrophotometric measurements.

	λ		340	350	390	460	525	550 mμ	
	$\varepsilon_{Cren_3^{+++}}$		51.3	60.7	16.0	75.6	6.2	1.6	
	$\varepsilon_{Cren_2(OH)_2^+}$		16.0	30.3	54.0	24.6	57.6	51.8	
	$\varepsilon_{Cren_3^{+++}} - \varepsilon_{Cren_2(OH)_2^+}$		35.3	30.4	−38.0	51.0	−51.4	−50.2	
		t h							Av.
1	$\varepsilon_0-\varepsilon_t$	239	18.0	16.2	−18.8	23.9	−26.9	−24.7	
	a	239	0.510	0.533	0.495	0.469	0.523	0.492	0.50
	$\varepsilon_0-\varepsilon_t$	334	21.0	18.8	−24.1	30.4	−32.8	−30.6	
	a	334	0.595	0.618	0.634	0.596	0.638	0.609	0.62
	$\varepsilon_0-\varepsilon_t$	624	27.9	24.7	−33.8	40.9	−43.9	−42.1	
	a	624	0.790	0.812	0.889	0.802	0.854	0.838	0.83
	$\varepsilon_0-\varepsilon_t$	1 727	33.4	28.1	−39.9	50.2	−49.8	−49.2	
	a	272	0.946	0.924	1.05	0.984	0.969	0.980	0.98
	$\varepsilon_0-\varepsilon_t$	1 800	34.2	29.4	−40.8	51.0	−51.2	−51.0	
	a	1 800	0.969	0.966	1.07	1.00	0.996	1.03	1.01
2	$\varepsilon_0-\varepsilon_t$	1 147	32.6	27.3	−39.3	48.3	−48.6	−47.6	
	a	1 147	0.924	0.898	(1.03)	0.946	0.945	0.948	0.93
	$\varepsilon_0-\varepsilon_t$	5 220			−39.2	50.6	−51.4	−50.9	
	a	5 220			1.03	0.992	1.01	1.00	1.01
	$\varepsilon_0-\varepsilon_t$	11 500			−39.2	53.6	−51.0	−50.8	
	a	11 500			1.03	1.05	1.00	1.01	1.02

The results of calculating a from (1) at suitable wavelengths inserting the *cis-trans* equilibrium values of $\varepsilon_{Cren_2(OH)_2^+}$ are given in Table 7. Here, the quantity $\frac{D_0-D_a}{l \times C_{Cr}}$ has been designated $\varepsilon_0-\varepsilon_t$. From the data concerning solution No. 1 it may be concluded that the primary reaction is an almost complete conversion of $Cren_3^{+++}$ into $Cren_2(OH)_2^+$. But the solution thus formed is not a true equilibrium solution, as its spectrum continues to change very slowly so that the absorption in the ultraviolet increases while the band at 19 000 cm^{-1} moves towards longer wavelengths and decreases slightly. This behaviour is typical of most of the solutions investigated.

In solution No. 2 the buffer concentration has been increased. Also in this medium $Cren_3^{+++}$ is almost completely converted into $Cren_2(OH)_2^+$, but the following changes in the spectrum are extremely slow (the spectrum was practically unchanged for a year except for a slight increase in the ultraviolet). It may therefore be assumed that the desired equilibrium has very nearly been established in this solution. The accuracy of the spectrophotometric measurements, however, does not permit a determination of $[Cren_3^{+++}]$.

An attempt was therefore made to determine this concentration chromatographically. It was shown that when a mixture of the trisethylenediamine and the *trans-* and *cis*-dihydroxo ions was chromatographed on a column of Al_2O_3 using 0.1 M KOH, 1 M KCl as an eluent, the three ions were clearly separated and eluated in the said order. 20 ml of solution No. 2 were chromatographed this way and all of the apparently colourless effluent (*ca.* 30 ml) leaving the column in front of the *trans* band was collected. The optical density of this effluent in an absorption cell with a 10 cm light path was recorded by the Cary whereby it should be possible to ascertain the presence of $Cren_3^{+++}$ in concentrations down to about 7×10^{-5} mole/l which would give rise to the optical density 0.05 at the maximum of the highest absorption band. However, the optical density observed was smaller than this, and it would hardly be safe to draw any other conslusion from the experiment than that $[Cren_3^{+++}]$ in the effluent was below 5×10^{-5} mole/l and in solution No. 2 therefore below 7.5×10^{-5} mole/l corresponding to $\alpha \sim 99.5$ %.

Although it is impossible to determine the stability constant k_3 from the present experiments, it is still of some interest to estimate its maximum value. Using the data of solution No. 2 in Table 7 at $t = 5\,220$ h: $-\log[H^+] = 9.85$, $[en] = 0.16$ (calculated under the assumption that one molecule en has been split off by the $Cren_3^{+++}$), $[OH^-] = 1.07 \times 10^{-4}$ (calculated using for the ionic concentration product of water, $k_{H_2O} = 10^{-13.82}$, the value given by Bjerrum and Unmack [12] for 1 M KCl at 25°C) and $\alpha \geqq 99.5$ %, this may be done as follows. Let us define a hydrolysis constant for $Cren_3^{+++}$

$$k_{h,1} = \frac{[Cren_2(OH)_2^+]\,[en]}{[Cren_3^{+++}]\,[OH^-]^2} = \frac{\alpha\,[en]}{(1-\alpha)\,[OH^-]^2}$$

Inserting the above values, we obtain $k_{h,1} \geqq 3 \times 10^5$ (Co 1.76). The corresponding constants $k_{h,1}(cis)$ and $k_{h,1}(tr.)$ are connected through

$$k_{h,1}(cis) + k_{h,1}(tr.) = k_{h,1} \text{ and } \frac{k_{h,1}(cis)}{k_{h,1}(tr.)} = q_2$$

Thus $k_{h,1}$ $(cis) \geqq 2.5 \times 10^5$ (Co 0.78) and $k_{h,1}$ $(tr.) \geqq 5 \times 10^4$ (Co 0.98). k_3 is related to these quantities through

$$k_3 = \frac{k_{s,1} \cdot k_{s,2}}{k_{h,1} \cdot k_{H_2O}^2}$$

In Ref.[1] k_3 for the cobalt(III) ethylenediamine system has erroneously been calculated from

$$k_3 = \frac{k_{h,1} \cdot k_{s,1} \cdot k_{s,2}}{k_{H_2O}^2}$$

Due to the fact that in the cobalt system $k_{h,1}$ is not very far from unity (when measured in liter/mole) the errors thus introduced are fortunately relatively small. The corrected values are given in parenthesis below.*

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* As a consequence of these corrections the quantities calculated for the cobalt (III) ethylenediamine system at ionic strength, $\mu = 1$ and 30°C (Table 1 of Ref. 1) should be changed as follows:

$\log k_1 = 19.2$ $\log k_2 = 16.2$ $\log k_3 = 13.31$ $\beta_1 = 1986$ $\beta_2 = 137$

Inserting the appropriate constants, we arrive at

$$k_3(cis) \leqq 10^{10.2} \text{ (Co } 10^{13.50}) \; k_3(tr.) \leqq 10^{11.3} \text{ (Co } 10^{15.26})$$

and defining $k_3(gr.)$ as k_3 for a system in *cis-trans* equilibrium so that

$$\frac{1}{k_3(cis)} + \frac{1}{k_3(tr.)} = \frac{1}{k_3(gr.)}$$

we obtain

$$k_3(gr.) \leqq 10^{10.2} \text{ liter/mole (Co } 10^{13.49}).$$

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