Reversible Isomerization Reactions of Di-μ-hydroxo-bis[*fac*-triamineaquachromium(III)] Ions in Aqueous Solution

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The dinuclear hydroxo-bridged chromium(III) complexes, the diols *trans*-$[(H_2O)L_3Cr(OH)_2CrL_3(H_2O)]^{4+}$ (Dt^{4+}) and *cis*-$[(H_2O)L_3Cr(OH)_2CrL_3(H_2O)]^{4+}$ (Dc^{4+}) with their once and twice deprotonated forms were shown to be in reversible equilibrium with each other in aqueous solution. L_3 was facially coordinated $(NH_3)_3$ or 1,4,7-triazacyclononane (tacn) and *cis* and *trans* refer to the position of the terminal water ligands relative to the $Cr(OH)_2Cr$ plane. With L_3 = $(NH_3)_3$ the main species at $[H^+]$ > *ca.* 0.5 M is the mono-ol $[(H_2O)_2(NH_3)_3Cr(OH)Cr(NH_3)_3(H_2O)_2]^{5+}$ (M^{5+}). Different salts of the *cis*- and *trans*-isomers and of M^{5+} were isolated.
In 1.0 M $NaClO_4/HClO_4$ at 25.0 °C the following molar concentration equilibrium constants were determined (K_1, K_2 and K_3 refer to the first, second and third acid dissociation constant, respectively): tacn system: pK_1 = 5.08 and 2.82, pK_2 = 7.25 and 8.80 for the *trans*- and *cis*-isomer, respectively, and $[Dc^{4+}]/[Dt^{4+}]$ = 0.037. For the NH_3 system the corresponding values are 6.15, 4.19, 7.48, 9.05 and 0.09, respectively. For M^{5+} $pK_1 \approx 1.5$, $pK_2 = 5.52$, $pK_3 = 8.18$ and $[M^{4+}]/[Dt^{4+}] \approx 0.04$. The low pK_1 values of Dc^{4+} and M^{5+} can be explained by intramolecular hydrogen bonding between terminally coordinated OH^- and H_2O. Thus the main species in the pH interval 5–8 is Dc^{3+} in these equilibria between the dimers.

The preparation, characterization and X-ray structure analysis of the *trans*-aquahydroxo-di-μ-hydroxo-bis[*fac*-triaminechromium(III)] ion, *trans*-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH)]^{3+}$ were presented in a recent paper[1] (*trans* refers to the position of the terminal OH^- and H_2O relative to the $Cr(OH)_2Cr$ bridge plane). It was herein pointed out that in aqueous solution this *trans*-diol, with its conjugate acid and base, is reversibly transformed into other species, in acid solution probably to the mono-ol ion, $[(H_2O)_2(NH_3)_3Cr(OH)Cr(NH_3)_3(H_2O)_2]^{5+}$.

Since then we have studied the equilibria which this diol ion gives rise to in aqueous solution, and in order to circumvent the problems connected with loss of ammonia in basic solutions as well as for comparative reasons we have studied the same system with other triamines as well, and 1,4,7-triazacyclononane (tacn) turned out to be a useful facially coordinating tridentate ligand in this connection. The investigaton has also led to the synthesis of some new compounds and to slight modifications of the synthesis of known ones.

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Results

This investigation concerns dimers obtained by condensation of *fac*-$CrL_3(H_2O)_3^{3+}$ with base. With L_3 being facially coordinated $(NH_3)_3$ or tacn four hydroxo-bridged dimers with the formula $[Cr_2(L_3)_2(OH)_3(H_2O)_n]^{3+}$ are possible, namely

$(OH)(H_2O)L_3Cr(OH)CrL_3(H_2O)(OH)^{3+}$
mono-ol, M^{3+}
trans-$(H_2O)L_3Cr(OH)_2CrL_3(OH)^{3+}$
trans-diol, Dt^{3+}
cis-$(H_2O)L_3Cr(OH)_2CrL_3(OH)^{3+}$
cis-diol, Dc^{3+}
(*trans*-diol and *cis*-diol together: D^{3+})
$L_3Cr(OH)_3CrL_3^{3+}$
triol

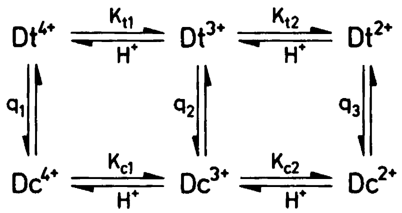
of which M^{3+} and D^{3+} have protonated as well as deprotonated forms. Prior to this investigation only salts of the *trans*-dimers were available, and the configuration determined, both with $L_3 = (NH_3)_3$[1] and with L_3 = tacn.[2]

From these salts we prepared salts of the *cis*-isomers according to the reaction

$$Dt^{4+} \overset{OH^-}{\rightleftharpoons} Dc^{3+}$$

as described in the experimental section.

With these compounds in hand we investigated the following reversible reactions:



Scheme 1

The pH measurements, described in more detail in the experimental section, show that in the pH range 3–10 (1.0 M $NaClO_4$, 25.0 °C) the tacn system behaves very similarly to the NH_3 system (except for the disturbing loss of NH_3 at pH > *ca.* 6). Immediately after dissolution the two isomers behave as dibasic acids with a charge of 4+ and after equilibration they behave as 4+ charged dibasic acids with intermediate acid dissociation constants from which the cis:trans ratios could be determined. The results of these measurements are given in Table 1 and Fig. 1 in the form of equilibrium constants and distribution curves.

In more acid media in the NH_3 system we detected and isolated the mono-ol. This complex is in equilibrium with the *cis*- and *trans*-diols and the relevant equilibrium constants were determined as described in the experimental section and are given in Table 1.

The assignment of the complexes is justified by these results. However, a few comments might be appropriate: The spectral behaviour (ESR and UV/VIS) and ion-exchange separations of equilibrated solutions (see experimental section) are in accordance with the obtained results and showed no signs of other species such as complexes of higher nuclearity (unlikely, also, because of the low, millimolar, chromium concentration) or monomers (ESR would show even traces of *fac*-$Cr(NH_3)_3(H_2O)_3^{3+}$, *e.g.*[3]). The pH measurements show that the triol cannot be present in detectable amounts. Nor were there any spectral signs of this complex (see the discussion section). Finally, the magnitude of the pK values and the similarity between the tacn and the NH_3 system make it very unlikely that the NH_3 ligands should be meridionally coordinated. All the NH_3 dimers are hydrolyzed to *fac*-$[Cr(NH_3)_3(H_2O)_3](ClO_4)_3$ with 70 % $HClO_4$.[1]

Table 1. Equilibrium constants determined in this investigation in 1.0 M $NaClO_4(HClO_4)$ at 25.0 °C. The dimension of the K values is mol · l⁻¹.

Equilibrium	NH_3 system	tacn system
$Dt^{4+} \rightleftharpoons Dt^{3+} + H^+$	pK_{t1}: 6.15(5)	5.08(2)
$Dt^{3+} \rightleftharpoons Dt^{2+} + H^+$	pK_{t2}: 7.48(5)	7.25(3)
$Dc^{4+} \rightleftharpoons Dc^{3+} + H^+$	pK_{c1}: 4.19(3)	2.82(3)
$Dc^{3+} \rightleftharpoons Dc^{2+} + H^+$	pK_{c2}: 9.05(3)	8.80(3)
$Dt^{4+} \rightleftharpoons Dc^{4+}$	q_1: 0.09(2)	0.037(3)
$Dt^{3+} \rightleftharpoons Dc^{3+}$	q_2: 8(2)	6.8(5)
$Dt^{2+} \rightleftharpoons Dc^{2+}$	q_3: 0.21(6)	0.19(2)
$M^{5+} \rightleftharpoons M^{4+} + H^+$	pK_{M1}: 1.5	
$M^{4+} \rightleftharpoons M^{3+} + H^+$	pK_{M2}: 5.52(5)	mono-ol
$M^{3+} \rightleftharpoons M^{2+} + H^+$	pK_{M3}: 8.18(6)	not
$Dt^{4+} \rightleftharpoons M^{4+}$	q: 0.04	observed
$M^{5+} \rightleftharpoons Dt^{4+} + H^+$	$pK_{M/Dt}$: 0.13	

Discussion

The magnitude of the acid dissociation constants and of the ratios between the isomers reflect the tendency to formation of intramolecular hydrogen bonds between terminal OH^- and H_2O. This phenomenon was primarily pointed out by Springborg *et al.*[4] on dimeric chromium(III) complexes with four nitrogen ligands *per* chromium atom and later confirmed by a crystal structure analysis[5] on a salt of the similar iridium(III) mono-ol $[(H_2O)en_2Ir(OH)Ir\,en_2(OH)]^{4+}$.

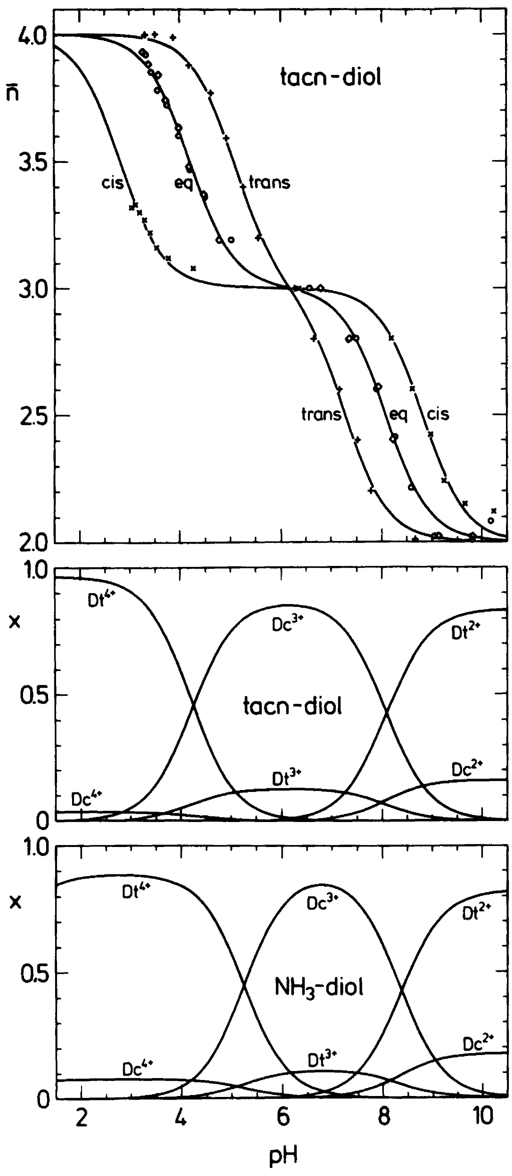


Fig. 1. Top: Mean charge, n̄, of the tacn dimers as a functuion of pH. × and ○ mark the experimental values at t = 0 and t = ∞, respectively, when starting with *cis*-diol; + and ◇ the corresponding values when starting with *trans*-diol. The curves are based on the calculated equilibrium constants given in Table 1. *Bottom:* Distribution curves for the tacn and NH_3 system: mole fraction as a function of pH derived from the calculated equilibrium constants (the curves for the mono-ol are not included).

Fig. 2 shows how the aquamono-ol by deprotonation forms such an intramolecular hydrogen bond and how the *cis*-diaquadiol has the same possibility.

In the mono-ol this stabilization of the conjugate base relative to the acid results in unusually high acid dissociation constants.[4] This phenomenon explains the observed differences between the pK_1 values of the *cis*- and *trans*-diols of the present investigations (*ca.* 2 pK units) as well as the low pK_{M1} of the mono-ol (Table 1).

As a consequence of this stabilization of Dc^{3+} the ratio $[Dc^{3+}]/[Dt^{3+}]$ is *ca.* 100 times bigger than the ratio $[Dc^{4+}]/[Dt^{4+}]$. The ratio $[Dc^{2+}]/[Dt^{2+}]$ is only a few times bigger than the ratio $[Dc^{4+}]/[Dt^{4+}]$ reflecting weaker hydrogen bonding in the Dc^{2+} ion compared to the Dc^{3+} ion.

The similarity between the tacn and the NH_3 system is pronounced and facilitated the investigation. Thus the distribution curves as function of pH are very similar (Fig. 1). The main difference arises from the difference between the K_{t1} values and between the K_{c1} values shifting the left side of the diagram *ca.* 1 pH unit towards higher pH for the NH_3 system. Furthermore, the formation of mono-ol must be considered (see the following section).

The mono-ol has, so far, not been observed for the tacn system. In the NH_3 system, however, it exists in equilibrium with the diols and in detect-

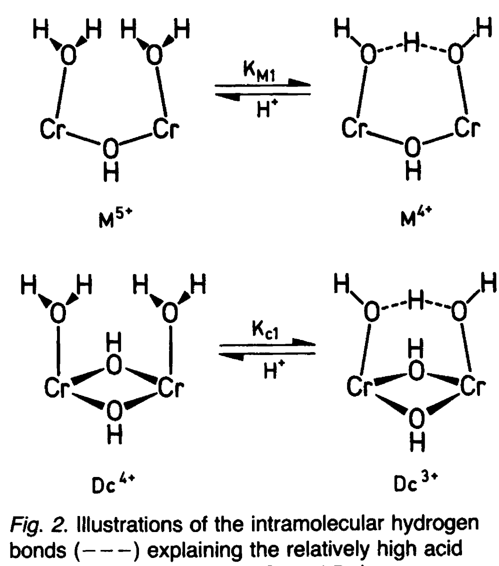


Fig. 2. Illustrations of the intramolecular hydrogen bonds (– – –) explaining the relatively high acid dissociation constants of M^{5+} and Dc^{4+}.

able amounts in acid media. M^{5+} is the main species at $[H^+] > ca. 0.5$ M and almost the only one in 4 M $HClO_4$ (80–90 %). The values of $pK_{M1} \approx 1.5$ and of $[M^{4+}]/[Dc^{4+}] \approx 0.5$ are comparable to those found for the tetraamine dimer (1.75 and 0.318, respectively).[4] With $pK_{M2} = 5.5$ and $pK_{M3} = 8.2$ the amount of mono-ol in the pH range 5–9 will not exceed *ca.* 2 % of the total amount of chromium and it was ignored in the determination of K_{eq1} and K_{eq2} (see experimental section).

Further aspects. Kinetic investigations in progress will throw more light on the cis/trans rearrangement observed here as well as on the mono-ol formation. In a recent paper[6] reactions involving rearrangements in polynuclear hydroxo-bridged aquachromium(III) complexes are discussed partly on the basis of the observations presented here. One aspect is that the cis/trans isomerization may occur directly and not *via* the mono-ol. We hope that the kinetic data will lead to a conclusion on this point now that we are able to isolate several salts of chromium dimers with a relatively high number of terminal water and hydroxo ligands.

Another aspect is that the triol has not been observed in the systems investigated here. Wieghardt *et al.*[7] isolated the chromium(III) triol with the 1,4,7-trimethylated tacn and observed some rather intense and narrow bands in the second d-d band in the absorption spectrum. In solutions brought to equilibrium with respect to *cis-* and *trans-*diol (tacn or NH_3) containing up to *ca.* 85 % Dc^{3+} we did not observe the slightest sign of such sharp maxima.

Experimental

Syntheses. Caution. In the following procedures handling of the perchlorates and of 70 % $HClO_4$ must be done with caution[8]: Preparations on a larger scale than prescribed should be avoided or done with the utmost care. Avoid scraping with a glass rod against sintered glass, avoid (local) heat, and dilute mixtures of organic solvents and 70 % $HClO_4$ at once. We did not experience explosions when these precautions were taken.

trans-$[(OH)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH)]I_2 \cdot 2H_2O$ (I) and salts of the protonated forms of this *trans*-diol. The prescriptions are given elsewhere.[1]

cis-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH)](ClO_4)_3 \cdot H_2O$ (II). 1.28 g of *trans*-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(H_2O)]I_4 \cdot 4H_2O$[1] was dissolved in 6.0 ml of water. Then 6 portions of 100 µl 1.5 M LiOH were added at 5 min intervals. After the last portion was added the solution was kept at room-temperature for 30 min. In this way the final pH was *ca.* 5.7 and the unwanted loss of NH_3 at higher pH was avoided while securing a high content of the *cis*-isomer. Next, 2.7 g of $LiClO_4$ were added in small portions, and the solution was kept at 0 °C for 15 min. The violet precipitate of *trans*-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH)](ClO_4)_3 \cdot aq$ was filtered off, and the solution was kept for crystallization at 0 °C for one day. The red crystals were filtered off, washed with ethanol and ether and air-dried. Yield: 200 mg of II (23 %). If this *cis*-isomer was contaminated by the *trans*-isomer the latter could be extracted with small portions of a 2:3 (v/v) mixture of water and saturated $LiClO_4$ solution.

$[(H_2O)_2(NH_3)_3Cr(OH)Cr(NH_3)_3(H_2O)_2](CF_3SO_3)_{3.7}(ClO_4)_{1.3} \cdot 1\frac{1}{2}H_2O$ (III). 370 mg of *trans*-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(H_2O)]I_4 \cdot 4H_2O$[1] were dissolved in 5 ml of 4 M $HClO_4$. The solution was kept at room temperature for 1 h after which the colour had changed from violet to red. Then 2 ml of CF_3SO_3H were added drop by drop under ice-cooling, and the solution was kept for crystallization at 0 °C for *ca.* 4 h. The red needles were filtered off and washed with ether until the washings were free of acid. Yield: 180 mg of III (41 %). The ratio of the anions could vary slightly.

1,4,7-triazacyclononane trihydrochloride (tacn · 3 HCl). The prescription is given elsewhere.[9]

trans-$[(H_2O)(tacn)Cr(OH)_2Cr(tacn)(H_2O)](ClO_4)_4 \cdot 4H_2O$ (IV). The prescription given by Wieghardt *et al.*[2] was modified in order to increase the hydrolysis rate of $Cr(tacn)Cl_3$: 3.7 g of this compound, prepared using a mixture of tacn · 3HCl and LiOH in a mole ratio 1:3 instead of tacn, were stirred with 31 ml of 1.2 M $AgClO_4$/0.1 M $HClO_4$ until the dark colour from the chlorocomplex disappeared. The solution should now be free of Ag^+. If not, some more $Cr(tacn)Cl_3$ should be added. The AgCl was filtered off, and the volume of the filtrate was reduced to 15 ml by evaporation. To the red solution 3.3 M LiOH was added drop by drop under stirring until pH = 6. The solution was kept for 1 h at room temperature, filtered and 4 M $HClO_4$ was added until pH = 2. Then solid $LiClO_4$ was added until precipitation began (*ca.* 2 g), and the solution was kept at 0 °C for 30 min for crystallization. The violet precipitate was filtered off, washed with ethanol and ether and air-dried. Yield: 2.2 g of IV (38 %).

trans-[(OH)(tacn)Cr(OH)$_2$Cr(tacn)(OH)](ClO$_4$)$_2$ · 1½H$_2$O (V). 0.4 g of IV was dissolved in 1.7 ml of ice-cold 0.55 M LiOH. 0.2 g of $LiClO_4$ was added immediately, and the red-violet crystals were filtered off, washed with ethanol and ether and air-dried. Yield: 0.23 g of V (79 %).

cis-[(H$_2$O)(tacn)Cr(OH)$_2$Cr(tacn)(OH)]I$_3$ · 3H$_2$O (VI). 1.0 g of IV was dissolved in 4.0 ml of water and 3.3 M LiOH was added until pH = 6.2. The solution was kept for 3 h at room temperature (pH changed only slightly) after which solid NaI was added until precipitation began (*ca.* 0.6 g). The red-violet precipitate was filtered off, washed with ethanol and ether and air-dried. Yield: 420 mg of crude *cis*-[(H$_2$O)(tacn)Cr(OH)$_2$Cr(tacn)(OH)]I$_3$ · 3H$_2$O. For reprecipitation 420 mg of the crude iodide were dissolved in 3.5 ml of water, and a saturated NaI solution was added drop by drop until crystallization began. The mixture was kept for *ca.* 30 min at 0 °C after which the precipitate was filtered off, washed with ethanol and ether and air-dried. Yield: 360 mg of VI (38 %).

Chemicals and chemical analyses. The chemicals were of reagent grade or of a similar or better quality. The synthesized compounds were analysed on a microscale for C, H, N, S, Cl, I, and Cr, and the analyses were, within 1–2 % relative, in accordance with the formulae given.

Apparatus. Visible absorption spectra were measured on a Cary 118 spectrophotometer and ESR-spectra on a Jeol JES-ME-1X instrument. A Perkin-Elmer 403 instrument was used for atomic absorption spectrophotometry.

pH measurements. The instrument was a Radiometer PHM 52 with a G 403 C glass electrode and a K 401 calomel electrode with 1.0 M NaCl in the salt bridge. Measurements were made in 1.0 M $NaClO_4$ at 25.0 ± 0.1 °C under stirring and under nitrogen atmosphere and shielded from light when necessary. The reliability of the system was controlled by titrations of $HClO_4$ with NaOH. The data from these titrations were fitted (pH versus µl titrant) by least squares refinement regarding the inclination and pH displacement of the glass electrode, sodium error, the ionization product of water, K_w (determined to $10^{-13.80}$ M^2 under these conditions) and carbonate content. The reproducibility was 0.01 pH unit within 1 min after dissolution of a sample.

Determination of the acid dissociation constants of trans- and cis-diol and of the cis:trans ratios. The reactions investigated are given in Scheme 1. Due to the cis/trans isomerization it was not possible to get a reliable determination of the acid dissociation constants from simple titrations of the isomers. The system was therefore investigated point by point as follows: *Ca.* 20 µmol of the diol salt was added to 25 ml 1.0 M $NaClO_4$ to which an amount of $HClO_4$ or NaOH had been added in advance. pH was then measured at 25.0 °C as a function of time, t, under stirring and nitrogen atmosphere. The change in $[H^+]$ was nearly exponential in t and was followed for at least 7 "half-lives" (0.5–3 h).

Values of $pH_{t=0}$ (by extrapolation) and of $pH_{t=\infty}$ were obtained in this way in the pH range 3–10 starting with *trans*-diol as well as with *cis*-diol, and with tacn as well as with NH_3 as ligand, *i.e.* salt I, II, V and VI. The loss of NH_3 in the latter case at higher pH gave rise to an increase in pH for which correction could be made. However, some of the $pH_{t=\infty}$ values for the NH_3 system are not too well defined and a few could not be determined at all.

Fig. 1 shows $\bar{n}$ as a function of pH for the tacn complexes where $\bar{n}$ is the mean charge on the diol: $\bar{n} = \{m_D \cdot n_D + V \cdot K_w/[H^+] + m_{HClO_4} - V \cdot [H^+] - m_{NaOH}\}/m_D$ where m_D, m_{HClO_4} and m_{NaOH} are the initial amount (µmol) of diol, $HClO_4$ and NaOH, respectively, n_D is the charge of the diol used, V is the total volume (µl) and K_w is the ionization product of water (= $10^{-13.80}$ M^2). From these data three pairs of acid dissociation constants were calculated by three separate least squares refinements: K_{t1} and K_{t2}, K_{c1} and K_{c2}, K_{eq1} and K_{eq2} where the last pair describes the equilibrium situation:

$$\bar{n} = \frac{4[H^+]^2 + 3K_1[H^+] + 2K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}$$

where K_1 and K_2 are the first and second acid dissociation constant, respectively. From

$$K_{eq1} = (K_{t1} + q_1K_{c1})/(1 + q_1)$$
$$K_{eq2} = (K_{t1}K_{t2} + q_1K_{c1}K_{c2})/(K_{t1} + q_1K_{c1})$$

final values of K_{t1}, K_{t2}, K_{c1}, K_{c2} and $q_1 = [Dc^{4+}]/[Dt^{4+}]$ were calculated by least squares refinement using the primarily derived three pairs of acid dissociation constants as experimental values (including their variance matrix elements) and the five last mentioned constants as parameters.

Values of $q_2 = [Dc^{3+}]/[Dt^{3+}]$ and of $q_3 = [Dc^{2+}]/[Dt^{2+}]$ were obtained using the relations $q_2 = q_1 \cdot K_{c1}/K_{t1}$ and $q_3 = q_2 \cdot K_{c2}/K_{t2}$.

The results for the tacn and the NH_3 complexes are given in Table 1 and Fig. 1.

When $HClO_4$ or NaOH was added to equilibrated solutions the resulting pH changes ($pH_{t=0}$ and $pH_{t=\infty}$) were in agreement with the obtained results.

Rapid cooling of equilibrated solutions to 0 °C followed by ion-exchange separation on Sephadex SE-C25 with 0.8 M $NaClO_4$ at 5 °C showed two bands: a reddish band of *cis*-diol followed by a violet one of *trans*-diol from solutions equilibrated at pH = 4–5 (tacn or NH_3 comples) and from solutions equilibrated at pH ≈ 8 (tacn complex) two bands in the reverse order (cf. the pK values). The chromium content in the two bands were in agreement with the results obtained from the pH measurements.

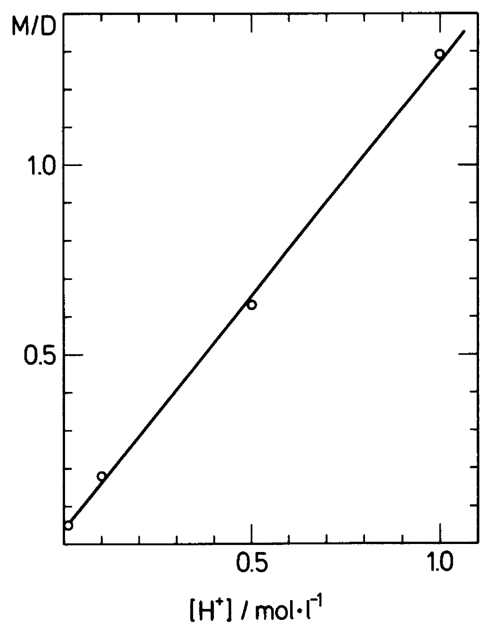


Fig. 3. M/D as a function of $[H^+]$, where M/D is the molar equilibrium ratio between $M = M^{5+}$ and $D = Dt^{4+} + Dc^{4+}$ for the NH_3 system as obtained from absorbance measurements at 520 nm. The solid line represents the constants given in Table 1.

Estimate of the ammonia mono-ol content. At pH 2–4 the UV/VIS spectral changes of solutions of Dt^{4+} are very small. At lower, constant pH, solutions of mono-ol and diol show distinct spectral changes in accordance with a pseudo first order reaction leading to equilibrium between these complexes ($t_{1/2}$ = 0.5 h at 25.0 °C in 0.5 M $HClO_4$/0.5 M $NaClO_4$). From the spectral changes (520 nm) in such solutions we obtained the equilibrium ratios, M/D, between mono-ol and diol in the pH interval 0–2 ($C_{HClO_4} + C_{NaClO_4} = 1.0$ M, 25.0 °C).

Fig. 3 shows the ratio M/D, calculated from these measurements, as a function of $[H^+]$. When it is assumed that the solutions contain only mono-ol, M (= $M^{5+} + M^{4+}$) and diol, D (= $Dt^{4+} + Dc^{4+}$) one has the relation $M/D = q' + q' \cdot [H^+]/K_{M1}$ where K_{M1} is the first acid dissociation constant of the mono-ol and $q' = [M^{4+}]/[D]$. The results are given in Table 1.

Rapid cooling of such equilibrated solutions to 0 °C followed by ion-exchange separation on Sephadex SP-C25 with 0.8 M $HClO_4$ at *ca.* 5 °C showed two not very well separated bands: a violet band of diol followed by a red one of mono-ol in a ratio which agreed with the spectral results.

The second and third acid dissociation constant, K_{M2} and K_{M3}, of the mono-ol were determined as described in the previous section from the M^{5+} salt (see Table 1).

Corresponding investigations of the tacn system showed no signs of the mono-ol after treatment for hours at 25 °C.

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