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

Peter Andersen*, Anders Døssing and Karen M. Nielsen

Department I, Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark


The dinuclear hydroxo-bridged chromium(III) complexes, the diols trans-[(H₂O)₃Cr(OH)₂CrL₂(H₂O)₂]⁺⁺ (Dt⁺⁺) and cis-[(H₂O)₃Cr(OH)₂CrL₂(H₂O)₂]⁺⁺ (De⁺⁺) with their once and twice deprotonated forms were shown to be in reversible equilibrium with each other in aqueous solution. L₂ was facially coordinated (NH₃)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 L₂ = (NH₃)₃, the main species at [H⁺] > ca. 0.5 M is the mono-ol [(H₂O)₃(NH₃)₃Cr(OH)₂Cr(NH₃)₃(H₂O)]⁺⁺ (M⁺⁺). Different salts of the cis- and trans-isomers and of M⁺⁺ were isolated. In 1.0 M NaClO₄/HClO₄ at 25.0°C the following molar concentration equilibrium constants were determined (K₁, K₂, and K₃ refer to the first, second and third acid dissociation constant, respectively): tacid system: pK₁ = 5.08 and 2.82, pK₂ = 7.25 and 8.80 for the trans- and cis-isomer, respectively, and [De⁺⁺]/[Dt⁺⁺] = 0.037. For the NH₃ system the corresponding values are 6.15, 4.19, 7.48, 9.05 and 0.09, respectively. For M⁺⁺ pK₁ = 1.5, pK₂ = 5.52, pK₃ = 8.18 and [M⁺⁺]/[De⁺⁺] ≈ 0.04. The low pK values of De⁺⁺ and M⁺⁺ can be explained by intramolecular hydrogen bonding between terminally coordinated OH⁻ and H₂O. Thus the main species in the pH interval 3–8 is De⁺⁺ 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-[(H₂O)₃(NH₃)₃Cr(OH)₂Cr(NH₃)₃(OH)]⁺⁺ were presented in a recent paper (trans refers to the position of the terminal OH⁻ and H₂O 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 acic solution probably to the mono-ol ion, [(H₂O)₃(NH₃)₃Cr(OH)Cr(NH₃)₃(H₂O)]⁺⁺.

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

*To whom correspondence should be addressed.

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.

Results

This investigation concerns dimers obtained by condensation of fac-CrL₂(H₂O)₃⁺⁺ with base. With L₂ being facially coordinated (NH₃)₃, or tacn four hydroxo-bridged dimers with the formula [Cr₃(L₂)(OH)(H₂O)]₆⁺⁺ are possible, namely

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$_3$)$_3$ and with L$_3$ = tacn.$^3$

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

\[ \text{Dt}^{4+} + \text{OH}^- \rightarrow \text{Dc}^{4+} \]

as described in the experimental section.

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

\[ \text{Dt}^{4+} + \text{H}^+ \leftrightarrow \text{Dt}^{3+} \]
\[ \text{Dt}^{3+} + \text{H}^+ \leftrightarrow \text{Dt}^{2+} \]
\[ \text{Dc}^{4+} + \text{H}^+ \leftrightarrow \text{Dc}^{3+} \]
\[ \text{Dc}^{3+} + \text{H}^+ \leftrightarrow \text{Dc}^{2+} \]

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$_2$O)$_2$$^{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$_2$O)$_3$] (ClO$_4$)$_3$ with 70 % HClO$_4$.$^1$

### 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$_2$O. 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$_2$O)en$_3$Ir(OH)Ir en$_3$(OH)]$^{4+}$.

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>NH$_3$ system</th>
<th>tacn system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dt$^{4+}$ ⇌ Dt$^{3+}$ + H$^+$</td>
<td>pK$_{a1}$: 6.15(5)</td>
<td>5.08(2)</td>
</tr>
<tr>
<td>Dt$^{3+}$ ⇌ Dt$^{2+}$ + H$^+$</td>
<td>pK$_{a2}$: 7.48(5)</td>
<td>7.25(3)</td>
</tr>
<tr>
<td>Dc$^{4+}$ ⇌ Dc$^{3+}$ + H$^+$</td>
<td>pK$_{a1}$: 4.19(3)</td>
<td>2.82(3)</td>
</tr>
<tr>
<td>Dc$^{3+}$ ⇌ Dc$^{2+}$ + H$^+$</td>
<td>pK$_{a2}$: 9.05(3)</td>
<td>8.80(3)</td>
</tr>
<tr>
<td>Dt$^{4+}$ ⇌ Dc$^{4+}$</td>
<td>q: 0.09(2)</td>
<td>0.037(3)</td>
</tr>
<tr>
<td>Dt$^{3+}$ ⇌ Dc$^{3+}$</td>
<td>q: 8(2)</td>
<td>6.8(5)</td>
</tr>
<tr>
<td>Dt$^{2+}$ ⇌ Dc$^{2+}$</td>
<td>q: 0.21(6)</td>
<td>0.19(2)</td>
</tr>
<tr>
<td>M$^{5+}$ ⇌ M$^{4+}$ + H$^+$</td>
<td>pK$_{a}$: 1.5</td>
<td></td>
</tr>
<tr>
<td>M$^{4+}$ ⇌ M$^{3+}$ + H$^+$</td>
<td>pK$_{a}$: 5.52(5)</td>
<td>mono-ol</td>
</tr>
<tr>
<td>M$^{3+}$ ⇌ M$^{2+}$ + H$^+$</td>
<td>pK$_{a}$: 8.18(6)</td>
<td>not</td>
</tr>
<tr>
<td>Dt$^{4+}$ ⇌ M$^{4+}$</td>
<td>q: 0.04</td>
<td>observed</td>
</tr>
<tr>
<td>M$^{5+}$ ⇌ Dt$^{4+}$ + H$^+$</td>
<td>pK$_{a}$: 0.13</td>
<td></td>
</tr>
</tbody>
</table>

143
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. This phenomenon explains the observed differences between the pH values of the cis- and trans-diols of the present investigations (ca. 2 pH units) as well as the low pKₘ₁ of the mono-ol (Table 1).

As a consequence of this stabilization of Dc³⁺, the ratio [Dc³⁺]/[Dt³⁺] is ca. 100 times bigger than the ratio [Dc⁴⁺]/[Dt⁴⁺]. The ratio [Dc³⁺]/[Dt²⁺] is only a few times bigger than the ratio [Dc⁴⁺]/[Dt⁴⁺] reflecting weaker hydrogen bonding in the Dc²⁺ ion compared to the Dc³⁺ ion.

The similarity between the tacn and the NH₃ 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 Kₘ₁ values and between the Kₘ₂ values shifting the left side of the diagram ca. 1 pH unit towards higher pH for the NH₃ 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 NH₃ system, however, it exists in equilibrium with the diols and in detect-

![Fig. 1. Top: Mean charge, n, of the tacn dimers as a function of pH. x 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 NH₃ system: mole fraction as a function of pH derived from the calculated equilibrium constants (the curves for the mono-ol are not included).](image_url)

![Fig. 2. Illustrations of the intramolecular hydrogen bonds (——) explaining the relatively high acid dissociation constants of M⁺⁺ and Dc⁴⁺.](image_url)
able amounts in acid media. Mf+ is the main species at [H+] > ca. 0.5 M and almost the only one in 4 M HClO4 (80–90%). The values of pH = 1.5 and of [Mf+]/[Dc+] ≈ 0.5 are comparable to those found for the tetraamine dimer (1.75 and 0.318, respectively). With pKm = 5.5 and pKm = 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 Kole and Kole (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 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 hydroxyl ligands.

Another aspect is that the triol has not been observed in the systems investigated here. Wieghardt et al. 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 NH3) containing up to ca. 85% Dc+ 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% HClO4 must be done with caution: 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% HClO4 at once. We did not experience explosions when these precautions were taken.

trans-[(OH)(NH3)2Cr(OH)2Cr(NH3)3(OH)]2·2H2O (I) and salts of the protonated forms of this trans-diol. The prescriptions are given elsewhere.

145
stirring until pH = 6. The solution was kept for 1 h at room temperature, filtered and 4 M HClO₄ was added until pH = 2. Then solid LiClO₄ 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)₂Cr(tacn)(OH)]
(ClO₄)₂·1/2H₂O (V). 0.4 g of IV was dissolved in 1.7 ml of ice-cold 0.55 M LiOH. 0.2 g of LiClO₄ 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-[(H₂O)(tacn)Cr(OH)₃Cr(tacn)(OH)]I₃·3H₂O (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-[(H₂O)(tacn)Cr(OH)₃Cr(tacn)(OH)]I₃·3H₂O. 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 NaClO₄ 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 HClO₄ 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, Kₙ (determined to 10⁻¹³.80 M² 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 NaClO₄ to which an amount of HClO₄ 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 pHₑₒ (by extrapolation) and of pHₑₚ 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 NH₃ as ligand, i.e. salt I, II, V and VI. The loss of NH₃ in the latter case at higher pH gave rise to an increase in pH for which correction could be made. However, some of the pHₑₒ values for the NH₃ system are not too well defined and a few could not be determined at all.

Fig. 1 shows n as a function of pH for the tacn complexes where n is the mean charge on the diol: n = (mₒ + ν·Kᵥ[H⁺] + mₜ₅[H⁺] + mₜ₅[H⁺] + mₜ₅[H⁺]) / mₒ, where mₒ, mₜ₅[H⁺] and mₜ₅[H⁺] are the initial amount (µmol) of diol, HClO₄ and NaOH, respectively, nₒ is the charge of the diol used, V is the total volume (µl) and Kᵥ is the ionization product of water (= 10⁻¹³.80 M²). From these data three pairs of acid dissociation constants were calculated by three separate least squares refinements: Kᵥ₁ and Kᵥ₂, Kᵥ₃ and Kᵥ₄, and Kᵥ₅ and Kᵥ₆, where the last pair describes the equilibrium situation:

n = 4[H⁺]³ + 3Kᵥ[H⁺] + 2KᵥKᵥ₂
[H⁺]³ + Kᵥ[H⁺] + KᵥKᵥ₂

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

Kᵥ₁ = (Kᵥ₁ + q₁Kᵥ₁)/(1 + q₁)
Kᵥ₂ = (Kᵥ₁Kᵥ₂ + q₁Kᵥ₁Kᵥ₂)/(Kᵥ₁ + q₁Kᵥ₁)
final values of $K_{11}$, $K_{12}$, $K_{21}$, $K_{22}$ and $q_1 = [\text{De}^{4+}] / [\text{Di}^{4+}]$ 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 $q_2 = [\text{De}^{3+}] / [\text{Di}^{4+}]$ and of $q_3 = [\text{De}^{2+}] / [\text{Di}^{4+}]$ were obtained using the relations $q_2 = q_1 \cdot K_{11} / K_{12}$ and $q_3 = q_2 \cdot K_{22} / K_{21}$.

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 ($\text{pH}_{\text{tacn}}$ and $\text{pH}_{\text{NH}_3}$) 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 redish band of cis-diol followed by a violet one of trans-diol from solutions equilibrated at pH = 4–5 (tacn or NH$_3$ complex) 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.

Estimate of the ammonia mono-ol content. At pH 2–4 the UV/VIS spectral changes of solutions of Di$^{4+}$ 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$_4$ or 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 ($C_{\text{HClO}_4} + C_{\text{NaClO}_4} = 1.0$ 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$^{6+}$ + M$^{4+}$) and diol, D (= Di$^{4+}$ + De$^{4+}$) one has the relation M/D = q$^{'}$ + q$^{'}$·[H$^+$]/K$_{M}$, where K$_{M}$ 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$_{M_2}$ and K$_{M_3}$, of the mono-ol were determined as described in the previous section from the M$^{4+}$ salt (see Table 1).

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

Acknowledgements. For the initial investigations of the tacn diol 1 g of the perchlorate of the trans-diol was most kindly handed over to us by Dr. J. Springborg who had received it from Dr. K. Wieghardt. We are very grateful for this donation. We also thank Dr. J. Springborg and Dr. O. Mønsted for valuable discussions, Dr. O. Mønsted for his help with the numerical treatment of the data and K. Jørgensen for her contribution to the analytical work.

References


Received September 2, 1985.