

Amido-Bridged Dinuclear Chromium(III) Complexes with 1,4,7-Triazacyclononane

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The chemical properties of the amido-bridged chromium(III) complexes $[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_3\text{Cr}(\text{tacn})]^{3+}$ (**1**) (and its ammine analogue) and $[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2(\mu\text{-OH})\text{Cr}(\text{tacn})]^{3+}$ (**4**) (tacn = 1,4,7-triazacyclononane) have been investigated in aqueous solution (1 M NaClO₄ at 25 °C) with the emphasis on the cleavage of the amido bridges, and the cleavage and formation of the hydroxo bridge. The cleavage products (tacn system) are new doubly bridged dimers with two amido bridges, or one amido bridge and one hydroxo bridge, which were isolated as perchlorate salts.

The compounds **1** and **4** are extremely inert towards amido-bridge cleavage in neutral and basic solution. In acid solution the rate constant for the irreversible cleavage of one of the amido bridges follows the expression $k_{\text{obs}} = k[\text{H}^+]$ with k being ca. $2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C ($1 \times 10 \text{ M}^{-1} \text{ s}^{-1}$ for the ammine analogue of **1**). The cleavage of the hydroxo bridge in **4** is reversible with k_{obs} falling from 10^{-2} to 10^{-6} s^{-1} as pH increases from 0 to 13. All the parameters of the reaction scheme have been determined, showing, e.g., that the equilibrium ratio between **4** and *cis*- $[(\text{H}_2\text{O})(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2\text{Cr}(\text{tacn})(\text{OH})]^{3+}$ is ca. 200, in contrast to the trihydroxo-bridged analogue, which is unstable. The doubly bridged dimers with one non-bridging NH₃ ligand lose this ligand, presumably by an intramolecular mechanism, with a rate constant of ca. 10^{-5} s^{-1} (pH dependent) to produce triply and doubly bridged dimers.

In a recent paper¹ we presented the synthesis and structure of $\text{Na}[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2(\mu\text{-OH})\text{Cr}(\text{tacn})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ (tacn = 1,4,7-triazacyclononane) and some of the chemical properties of this new dinuclear chromium(III) complex. The complex can be synthesized from $[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_3\text{Cr}(\text{tacn})]^{3+}$ (**1**), and in the following we describe the aqueous chemistry of these complexes with the emphasis on the cleavage of amido bridges and the formation and cleavage of the hydroxo bridge. Bridge cleavage and formation have in the past been studied with purely hydroxo-bridged dinuclear chromium(III) complexes,^{2–4} and comparison with these systems is obvious.

The ammine analogue^{5,6} to **1**, $[(\text{NH}_3)_3\text{Cr}(\mu\text{-NH}_2)_3\text{-Cr}(\text{NH}_3)_3]^{3+}$, has been studied as well. Like **1** it undergoes cleavage of one amido bridge in acid aqueous solution. However, the steps following this cleavage are in this case difficult to interpret because of loss of ammonia from different positions in the complex, and only the first bridge cleavage step will be discussed here. Blocking one face in the octahedral coordination sphere

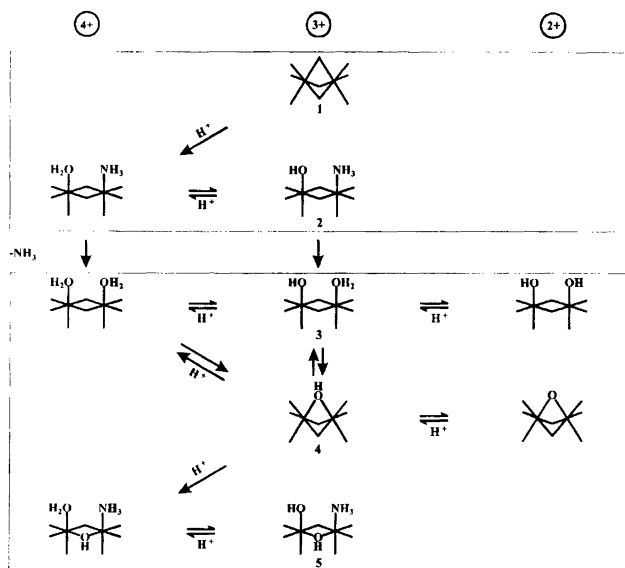
of chromium(III) with tacn has made the interpretation of the next steps possible. The combination of ion exchange chromatography (FPLC) and UV/VIS spectral measurements has been an efficient method to follow the reactions. As equilibrium data and kinetic data were obtained it became possible to design syntheses for most of the involved species in a pure crystalline state, and in this way provide better information about the system.

Results

Irreversible cleavage of one amido bridge in 1 and in the ammine analogue. The pH dependency of the pseudo-first-order rate constant, k_{obs} , for this bridge cleavage is shown in Fig. 1, and the resulting rate constants, k ($= k_{\text{obs}}/[\text{H}^+]$), and activation parameters are given in Table 1. The cleavage product, **2** + (cf. Scheme 1), irreversibly loses ammonia (see below).

Irreversible cleavage of one amido bridge in 4. This step is rather similar to the amido bridge cleavage of **1** (see above), and the pH dependency and the results are given

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Scheme 1. The scheme shows the observed reactions starting with $[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_3\text{Cr}(\text{tacn})]^{3+}$ (**1**) in 1.0 M (Na,H)- $(\text{ClO}_4, \text{OH})$. For clearness the tacn and the $\mu\text{-NH}_2$ groups have been omitted, and the ionic charges are given at the top of the scheme. The scheme is divided into two boxes, where the lower box contains species which have irreversibly lost one ammonia molecule compared to the species in the upper box. The numbering, n (**1** to **5**), of the species with charge $3+$ is used in the text, and in such a way that $n+$ is the protonated form of n , and $n-$ is the deprotonated form of n .

in a similar way in Fig. 1 and Table 1. The cleavage product, **5+**, irreversibly loses ammonia (see below).

Reversible cleavage/formation of the hydroxo bridge in 4. Besides the irreversible cleavage of one amido bridge in **4** (see above) a reversible cleavage/formation of the hydroxo bridge takes place. The pH dependency of $\log k_{\text{obs}}$ for this process is shown in Fig. 2, and a reaction scheme is proposed in Scheme 2 (analogous to schemes given earlier⁴).

The expression for the observed pseudo-first-order rate constant as a function of $[\text{H}^+]$ is given in eqn. (1) (cf. analogous schemes⁴).

$$k_{\text{obs}} = (k_{4+,3+}[\text{H}^+]^2 + k_{4,3}K_{1(4+)})[\text{H}^+] \times \{([\text{H}^+]^2 + K_{1(4+)}[\text{H}^+] + K_{1(4+)}K_{2(4+)})^{-1} + ([\text{H}^+]^2 + K_{1(3+)}[\text{H}^+] + K_{1(3+)}K_{2(3+)})^{-1}K_{4+,3+}^{-1}\} \quad (1)$$

Table 1. Rate constants, k ($=k_{\text{obs}}/[\text{H}^+]$), and activation parameters for the irreversible amido bridge cleavages **1** \rightarrow **2+** [tacn and the analogous *fac*-(NH_3)₃ complexes] and **4** \rightarrow **5+** (tacn complex) in 1.0 M (Na,H) ClO_4 at 25.0 °C (cf. Scheme 1 and Fig. 1).

	1 \rightarrow 2+		4 \rightarrow 5+ tacn
	<i>fac</i> -(NH_3) ₃	tacn	
$k/\text{M}^{-1} \text{s}^{-1}$	11.9(9) ^a	$2.64(6) \times 10^{-3}$	$1.72(10) \times 10^{-3}$
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	28(4)	65(2)	63(3)
$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	-129(13)	-76(8)	-85(10)

^a27.9(11) in 1.0 M NaBr.

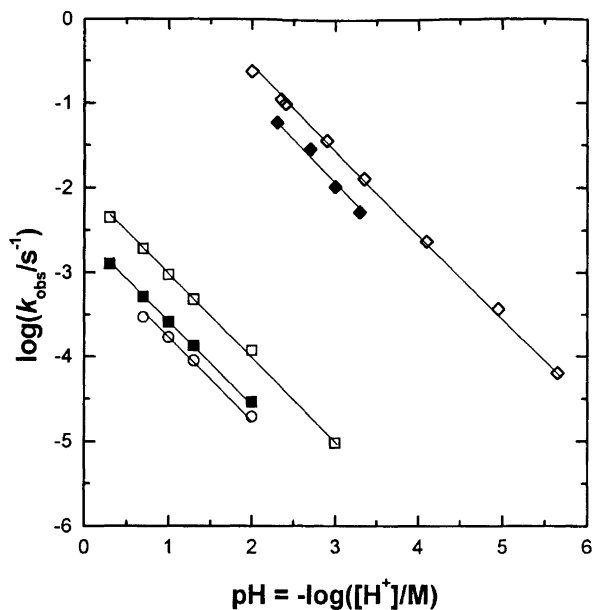
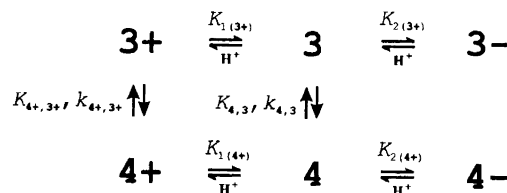


Fig. 1. Examples of acid-catalyzed amido bridge cleavage of $[\text{L}_3\text{Cr}(\mu\text{-NH}_2)_3\text{CrL}_3]^{3+}$ with $\text{L}_3 = (\text{NH}_3)_3$ in 1.0 M NaBr (\diamond) and in 1 M NaClO_4 (\blacklozenge) at 25.0 °C and with $\text{L}_3 = \text{tacn}$ in 1.0 M (Na,H) ClO_4 at 40.0 °C (\square) and at 25.0 °C (\blacksquare). The bottom curve (\circ) is for the amido bridge cleavage of $[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2(\mu\text{-OH})\text{Cr}(\text{tacn})]^{3+}$ in 1.0 M (Na,H) ClO_4 at 25.0 °C. The lines are the result of least squares refinements (unit weights) using $\log k_{\text{obs}} = -\text{pH} + \log k$ (the k -values are given in Table 1).



Scheme 2. The reaction scheme proposed for the reversible cleavage/formation of one hydroxo bridge in **4** (cf. Scheme 1). The species **4+** contains a water bridge (protonation of the hydroxo bridge in **4**), which is a strong acid, and therefore only the ratio $k_{4+,3+}/K_{1(4+)}$ can be determined. The $3- \rightleftharpoons 4-$ step was too slow for a determination of its rate constants, $k_{4-,3-}$ and $k_{3-,4-}$. With these exceptions all the other rate constants and equilibrium constants for this system have been determined from the kinetic data obtained from perchlorate salts of **4** and **3-** or solutions rich in **3-**.

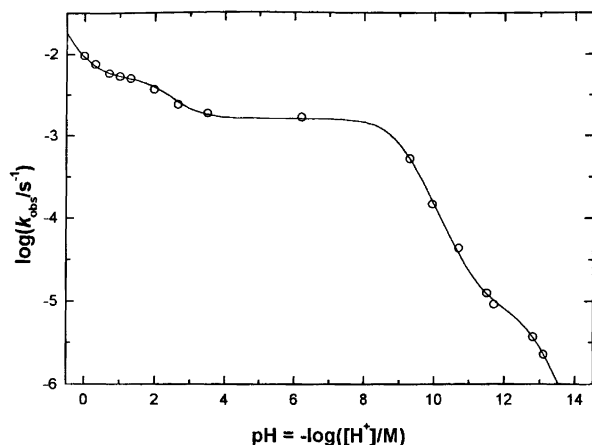


Fig. 2. $\log k_{\text{obs}}$ vs. pH for the reversible cleavage/formation of the hydroxo bridge in **4** (cf. Scheme 1) in 1.00 M (Na,H)(ClO₄,OH) at 25.0 °C. The curve is the result of least squares refinements (unit weights) using eqn. (1) and the calculated constants given in Table 2.

Least-squares refinements on the pH, $\log k_{\text{obs}}$ data (unit weights) using this equation gave the values for six parameters: $k_{4+,3+}/K_{1(4+)}$, $k_{4,3}$, $K_{4,3}$, and the acid dissociation constants $K_{1(3+)}$, $K_{2(3+)}$ and $K_{2(4+)}$. The curve in Fig. 2 is based on eqn. (1) with these six values, which are given in Table 2 together with other constants derived from them.

Some of the equilibrium constants in Table 2 could be confirmed in a more direct way. This applies for $pK_{2(4+)}$, which was determined to 12.7(1) from analysis of UV/VIS spectra of **4** in the pH interval 11.8–13.3 (cf. Fig. 3). A direct FPLC determination of the equilibrium ratio $([3+] + [3-]) / ([4+] + [4-])$ in acid and basic solutions was also, within the experimental error, in accordance with the equilibrium constants in Table 2: Figure 4 shows an example in acid solution, and at pH 11.4 this ratio was determined to 1.0 from both sides, compared to 1.2 from the constants of Table 2.

Loss of ammonia from the complexes. Figure 5 shows the pH dependency of $\log k_{\text{obs}}$, where k_{obs} is the observed rate constant for the irreversible loss of one ammonia molecule from **2+** or **2**. k_{obs} can be expressed as in

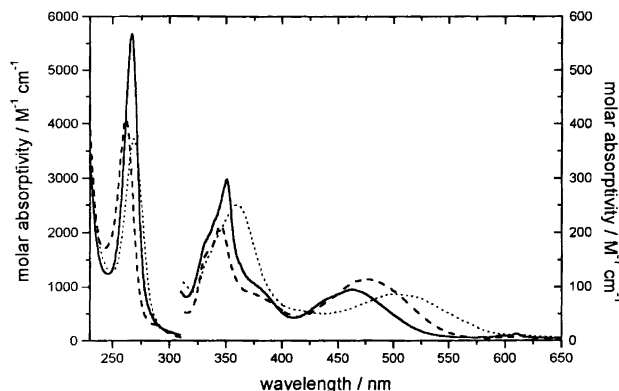


Fig. 3. UV/VIS spectra of **1** in H₂O (—), **4** in H₂O (---) and **4** in 1.0 M NaOH (.....).

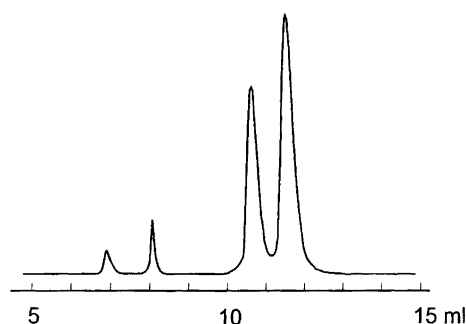


Fig. 4. FPLC diagram of **4** after 67 min in 0.10 M HClO₄/0.90 M NaClO₄ at 25.0 °C. The elution gradient is from H₂O (0 ml) to 1.0 M NaCl buffered with 0.02 M propane-1,3-diamine/0.002 M HCl (12 ml). The four peaks represent, from left to right, complex **6+** (5% of the total chromium content), **3+** (5%), **5+** (43%) and **4** (47%). **6+** is the complex obtained when **5+** loses one ammonia molecule. The chromium content, calculated from the rate constants determined by UV/VIS time-drives, are 4, 5, 41 and 50%, respectively.

eqn. (2), where k_1 and k_2 are the rate constants for the ammonia loss from **2+** and **2**, respectively, and $K_{1(2+)}$ is the acid dissociation constant of **2+**.

$$k_{\text{obs}} = (k_1[\text{H}^+]/K_{1(2+)} + k_2)/([\text{H}^+]/K_{1(2+)} + 1) \quad (2)$$

Least-squares refinements of the pH, $\log k_{\text{obs}}$ data (unit weights) using this expression determined the values

Table 2. Rate constants and equilibrium constants in 1.0 M NaClO₄ at 25.0 °C for the reversible cleavage/formation of the hydroxo bridge in **4** (cf. Schemes 1 and 2 and Fig. 2). For comparison some corresponding constants are given for [L₃Cr(μ-OH)₃CrL₃]³⁺ complexes.

	4 (this work)	L ₃ : (NH ₃) ₃ ^{9,11}	tacn ^{10,11}	Me ₃ -tame ^{4,a}
$k_{4+,3+}K_{1(4+)}^{-1}/\text{M}^{-1}\text{s}^{-1}$	$4.3(8) \times 10^{-3}$	3.4×10^3		7.1×10^{-3}
$k_{4,3}/\text{s}^{-1}$	$8.0(8) \times 10^{-6}$	3.6×10^{-2}	1.2×10^{-2b}	1×10^{-7}
$k_{3+,4+}/\text{s}^{-1}$	$5.1(2) \times 10^{-3}$			8×10^{-4}
$k_{3,4}/\text{s}^{-1}$	$1.6(1) \times 10^{-3}$			1.0×10^{-4}
$K_{4,3} = [3]/[4]$	$5.1(7) \times 10^{-3}$			1×10^{-3}
$K_{4-,3-} = [3-]/[4-]$	24(5)			
$pK_{1(3+)} = -\log(K_{1(3+)}/\text{M})$	2.22(10)	4.09	2.77	3.29
$pK_{2(3+)} = -\log(K_{2(3+)}/\text{M})$	8.99(4)	9.05	8.84	9.17
$pK_{2(4+)} = -\log(K_{2(4+)}/\text{M})$	12.67(7)			

^a1.0 M NaBr [Me₃-tame = *N,N',N''*-trimethyl-1,1,1-tris(aminomethyl)ethane]. ^bH₂O (extrapolated).

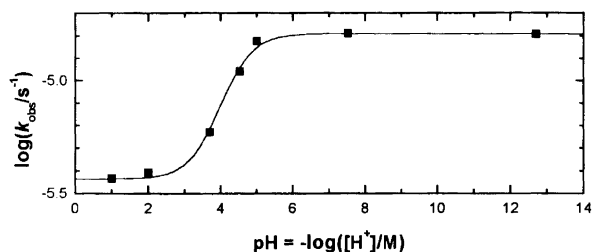


Fig. 5. $\log k_{\text{obs}}$ vs. pH for the irreversible loss of one ammonia molecule from **2+** or **2** in 1.00 M (Na,H)(ClO₄,OH) at 25.0 °C. The curve is the result of least squares refinements (unit weights) using eqn. (2) and the constants given in the text.

of the three parameters: $k_1 = 3.7(4) \times 10^{-6} \text{ s}^{-1}$, $k_2 = 16.2(1) \times 10^{-6} \text{ s}^{-1}$ and $\text{p}K_{1(2+)} = 4.31(8)$ [in 1.0 M (Na,H)(ClO₄,OH) at 25.0 °C]. By a direct acid–base titration of **2** $\text{p}K_{1(2+)}$ was determined to 4.33(1) (same medium and temperature).

In acid solution the products from the ammonia loss are the equilibrium mixture of **3+** and **4** going irreversibly into **5+**. In neutral solution the product is **4**, and the reaction $\mathbf{3} \rightleftharpoons \mathbf{4}$ could not be detected. At high pH (13) two exponential terms could be determined, i.e. the small rate constant for the $\mathbf{3} \rightleftharpoons \mathbf{4}$ equilibration via the species with charge 3+ (also determined starting with **4**, see above) and the, at this pH, larger rate constant for the loss of ammonia from **2**. However, the triply bridged complex is formed prior to the doubly bridged, as revealed by FPLC (see below).

The amidohydroxo-bridged complex **5** has properties rather similar to those of **2**. $\text{p}K_{1(5+)}$ was determined to 4.69(1) by a direct acid–base titration. Compound **5**, like **2**, loses one ammonia molecule with a pH-dependent rate constant of the same order of magnitude as for **2** (1.5×10^{-5} and $0.9 \times 10^{-5} \text{ s}^{-1}$ for k_1 and k_2 , respectively). The products are, as judged from FPLC and the UV/VIS spectra, the dinuclear complex with one amido bridge and two hydroxo bridges and the complex with one amido bridge and one hydroxo bridge. The doubly bridged complex shows two peaks on FPLC, probably the *cis*- and *trans*-isomer, where *cis* and *trans* refer to the position of the non-bridging H₂O or OH[−] ligands relative to the bridge plane. One of these isomers, probably the *trans*-isomer, has been isolated as [(H₂O)(tacn)Cr(μ-NH₂)(μ-OH)Cr(tacn)(H₂O)](ClO₄)₄ (see the discussion below on *cis*, *trans*-isomerism).

Discussion

Amido bridge cleavage. In acid aqueous solution the tacn complexes **1** and **4** (and the ammine analogue of **1**) undergo amido bridge cleavage, resulting in a doubly bridged dimer with a non-bridging water ligand on one chromium centre and an ammonia ligand on the other. The bridge cleavage is irreversible, as one might expect. While cobalt(III) under appropriate conditions is able to form amido bridges in aqueous ammonia solution,^{6,7}

chromium(III) seems to require anhydrous liquid ammonia conditions.

It is noteworthy that the [H⁺] dependency of the observed rate constants for the amido bridge cleavage follows the expression $k_{\text{obs}} = k[\text{H}^+]$ for these chromium(III) dimers. In neutral and basic solution **1** and **4** are extremely robust towards amido bridge cleavage.

An acid-catalyzed path for the cleavage of a hydroxo bridge between two chromium centres has been observed in several cases,^{2–4} where it can be explained by the formation of a protonated hydroxo bridge, i.e. an aqua bridge, which is a strong acid in aqueous solution. For the amido bridge cleavage a similar path involving a protonation of the amido bridge is not possible, since the nitrogen atom is coordinatively saturated. The rate constants for base-catalyzed and uncatalyzed paths, observed for hydroxo bridge cleavage in chromium(III) dimers,^{2–4,8–10} were not measured for the slow amido bridge cleavages.

Comparison of the acid-catalyzed bridge cleavage of [(NH₃)₃Cr(μ-NH₂)₃Cr(NH₃)₃]³⁺ and of [(NH₃)₃Cr(μ-OH)₃Cr(NH₃)₃]³⁺ (Tables 1 and 2) shows that k for the triamido-bridged complex is 3×10^2 times smaller than $k_{4+,3+} K_{1(4+)}$ ^{−1} (corresponding to k) for the trihydroxo-bridged complex. The decrease is due a ΔS^\ddagger decrease⁹ from 36 to $-129 \text{ J mol}^{-1} \text{ K}^{-1}$, while ΔH^\ddagger decreases from 64 to 28 kJ mol^{−1}.

The corresponding value of k for the tacn complex **1** is a further four orders of magnitude smaller, now mainly due to an increase of ΔH^\ddagger to 65 kJ mol^{−1}. Unfortunately there are no corresponding k data available for [(tacn)Cr(μ-OH)₃Cr(tacn)]³⁺. However, the rate constant for the uncatalyzed bridge cleavage of this complex in neutral solution is many orders of magnitude larger than for the amido bridge cleavage.¹⁰ The acid-catalyzed cleavage of one of the amido bridges in **4** takes place with nearly the same rate constant and activation parameters as for **1**, suggesting similar mechanisms. The exact nature of these acid-catalyzed bridge cleavages can only be speculative on the present basis. However, the fact that the bridge cleavage with the highest acid-catalyzed (and uncatalyzed) rate constant is found for [(NH₃)₃Cr(μ-OH)₃Cr(NH₃)₃]³⁺ agrees well with the fact that we here have an accessible lone-pair on the bridging atom, not protected by hydrophobic neighbouring ligands or hydrogen atoms from neighbouring amido bridges (see below).

Hydroxo bridge cleavage and formation. The reversible hydroxo bridge cleavage of **4** was studied over the entire pH interval 0–13. The results are given in Table 2, where they are compared with other relevant data.

$k_{4+,3+} K_{1(4+)}$ ^{−1} for the acid-catalyzed hydroxo bridge cleavage of **4** is only approximately twice the k -values for the amido bridge cleavage of **1** and **4**, and the rate constant for the uncatalyzed hydroxo bridge cleavage of **4**, $k_{4,3}$, is small compared to that of the trihydroxo-

bridged analogue.¹⁰ There is hardly any doubt that some of this inertness of the hydroxo bridge in **4**, approaching that in $[(\text{Me}_3\text{-tame})\text{Cr}(\mu\text{-OH})_3\text{Cr}(\text{Me}_3\text{-tame})]^{3+}$ (see below and Table 2), must be attributed to the presence of the two amido bridges. It is also noteworthy that there is no sign of a base-catalyzed path, even when the oxo-bridged form of **4** dominates, such as is observed for⁹ $[(\text{NH}_3)_3\text{Cr}(\mu\text{-OH})_3\text{Cr}(\text{NH}_3)_3]^{3+}$ and for⁸ $[(\text{tacd})\text{Cr}(\mu\text{-OH})_3\text{Cr}(\text{tacd})]^{3+}$ (tacd = 1,5,9-triazacyclododecane).

The high stability of **4** relative to **3** is also remarkable, when compared to the analogous trihydroxo-bridged complex,¹⁰ which is unstable relative to the dihydroxo-bridged *cis*-aqua-hydroxo dimer. The acid dissociation constants ($\text{p}K_{1(3+)}$ and $\text{p}K_{2(3+)}$, see Table 2) of the doubly bridged complexes, 6–7 $\text{p}K_{\text{a}}$ units apart, in both cases reveal a stabilizing $\text{H}-\text{O}-\text{H}\cdots\text{O}-\text{H}$ intramolecular hydrogen bond¹¹ in the *cis*-aqua-hydroxo dimer.

The structure¹ of **4** resembles those of trihydroxo-bridged chromium(III) dimers with respect to bond angles and distances. However, with respect to cleavage and formation of the hydroxo bridge, **4** resembles the trihydroxo-bridged dimer with $\text{Me}_3\text{-tame}$ much more than the unstable tacn analogue, let alone the ammine analogue (Table 2). The high stability and inertness of this $\text{Me}_3\text{-tame}$ complex have been connected⁴ to steric hindrance of the amine ligands in the doubly bridged cleavage product. In the present case with **4** (and **4**–) the presence of the two amido bridges apparently plays a significant role for the stability as well as for the inertness.

For the complex **4**, the competition between the irreversible cleavage of one of the amido bridges and the reversible cleavage of the hydroxo bridge governs the behaviour in aqueous solution as follows. In stronger acid solution formation of **3**+ favours this complex relative to **4** ($K = [\text{H}^+][\mathbf{4}]/[\mathbf{3}+] = 1.2 \text{ M}$). However, the competing amido bridge cleavage in this medium (7 min half-life at 25 °C with $[\text{H}^+] = 1 \text{ M}$) has the consequence that **5**+ is formed irreversibly along with the **3**+/**4** equilibration. With increasing pH the amido bridge cleavage becomes of minor importance, and **4** will dominate such solutions until pH 11 ($K = [\text{H}^+][\mathbf{3-}]/[\mathbf{4}] = 5 \times 10^{-12} \text{ M}$), where the equilibrium ratio between **4** and **3**– is ca. 1. The rate of equilibration in basic solution is much slower than in acid solution (cf. Fig. 2) and is established via **4** and not via its deprotonated $\mu\text{-O}$ form, **4**–, as judged from the continuously decreasing k_{obs} vs. pH.

Acid-base properties. The acid dissociation constants of the species are a useful indication of the composition of these dinuclear complexes. Their number will tell how many non-bridging water ligands the species have, and their magnitude may give configurational information as in the case of complex **3**+, where the acid dissociation constants tell, with high evidence, that this complex possesses two non-bridging water ligands with *cis*-con-

figuration.¹¹ The weaker monoprotic acids **2**+ and **5**+ ($\text{p}K_{\text{a}}$ 4.3 and 4.7, respectively) are slightly stronger acids than *trans*- $[(\text{H}_2\text{O})(\text{tacn})\text{Cr}(\mu\text{-OH})_2\text{Cr}(\text{tacn})(\text{H}_2\text{O})]^{4+}$ ($\text{p}K_{\text{a}} = 5.1$), perhaps because of the vicinity of a NH_3 ligand (owing to the way of formation, we believe that the NH_3 ligand is in *cis*-position relative to the non-bridging $\text{H}_2\text{O}/\text{OH}^-$, see below). The fact that the loss of ammonia from **2**+ and **2** can be correlated solely to the acid dissociation constant points to an intramolecular mechanism for this process. Finally, the magnitude of the acid dissociation constant of **4**, $\text{p}K_{\text{a}} = 12.6$, is close to the 12.9 found for the trihydroxo-bridged tacn chromium(III) dimer,⁸ while the acidity of an amido bridge must be expected to be lower.

cis, trans-Isomerization. All the doubly bridged complexes in Scheme 1 may in principle exist in a *cis*- and a *trans*-form, but for none of them was it possible to isolate more than one isomer, nor did two isomers show up on FPLC. For the dihydroxo-bridged complex, $[(\text{H}_2\text{O})(\text{tacn})\text{Cr}(\mu\text{-OH})_2\text{Cr}(\text{tacn})(\text{H}_2\text{O})]^{4+}$ (and the ammine analogue) and the deprotonated forms, it has earlier been demonstrated¹¹ that *cis, trans*-isomerization equilibria are obtained with rate constants of the magnitude $10^{-3}\text{--}10^{-2} \text{ s}^{-1}$, and that this isomerization takes place without formation of a monohydroxo-bridged complex. The proposed mechanism¹² for this isomerization involves the establishment of a bond from a non-bridging $\text{H}_2\text{O}/\text{OH}^-$ on one chromium centre to the other, with the consequence that a bond cleavage of the original hydroxo bridge is facilitated, possibly assisted by an intramolecular proton transfer. An analogous mechanism with loosening of an amido bridge seems not to take place. This is a support for the proposed mechanism, considering the higher inertness of the amido bridge. What can happen instead, as demonstrated for **2** in basic solution, is the formation of an extra bridge ($\mu\text{-OH}$), while a non-bridging ammonia molecule is dissociated.

Three products are observed when **5** loses an ammonia molecule. One of them has been isolated as $[(\text{H}_2\text{O})(\text{tacn})\text{Cr}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Cr}(\text{tacn})(\text{H}_2\text{O})](\text{ClO}_4)_4$ (see Experimental). From the FPLC behaviour we believe, by comparison with the analogous dihydroxo-bridged complexes, that this compound is the *trans*-isomer, and that the other two are the *cis*-analogue and the $[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)(\mu\text{-OH})_2\text{Cr}(\text{tacn})]^{3+}$ complex. In neutral solution they are present in comparable concentrations, i.e. this triply bridged complex is intermediate in stability between the very stable complex, **4**, and the unstable $[(\text{tacn})\text{Cr}(\mu\text{-OH})_3\text{Cr}(\text{tacn})]^{3+}$ ion. In other words the hydroxo-bridge stability of these triply bridged complexes increases with the number of amido bridges (or the stability with respect to hydroxo-bridge formation for the doubly bridged products decreases with the number of amido bridges). This system, where complex **1** has lost two ammonia molecules, is being investigated more detailed at present.

Dinuclear complexes with only one bridge were not

observed in the present tacn system as judged from the mutual behaviour of the involved species and their acid–base properties. Treatment with rather concentrated acid (and heating) will eventually give mononuclear species. A similar behaviour is observed for the dihydroxo-bridged chromium(III) dimers with tacn, but for ammine, ethane-1,2-diamine and aqua chromium(III) complexes, equilibria between mono- and dihydroxo-bridged dimers have been demonstrated.^{2,3,13}

Experimental

Chemicals and apparatus. The chemicals were of reagent grade or better quality. The synthesized compounds were analysed for Cr, C, H and N at our Department for Microanalysis, and the analyses were within 1–2% in accordance with the given formulae. The purity of the complexes were further controlled by FPLC (see below) to contain less than ca. 1% of related complexes.

UV/VIS spectral data (scans and time drives) were collected on a Perkin-Elmer Lambda40 instrument equipped with a thermostated cell chamber.

The ion-exchange liquid chromatography (FPLC) was performed on a Pharmacia instrument using a Mono HR 5/5 column with an elution gradient from water to 1 M NaCl buffered with 0.02 M propane-1,3-diamine/0.002 M HCl. Peak heights or, if necessary, peak areas were used for kinetic data (UV detection at 254 nm). The experimental details for the FPLC separations in connection with the present project have recently been described.¹

pH measurements were performed on a Radiometer PHM82 instrument with a PHC2406 electrode system. 1.00 M (Na,H)(ClO₄,OH) (or analogously NaBr) solutions were used to adjust pH in the intervals 1–4 and 10–13 (using pK_w = 13.80 in 1 M NaClO₄ at 25 °C). The acid dissociation constants were determined by regression analysis of acid–base titration data as described by Mønsted and Mønsted.¹⁴ The data were collected on a Radiometer PHM52 instrument equipped with a G202C glass electrode and a K401 calomel reference electrode with 1.0 M NaCl in the salt bridge.

Syntheses. Caution! In the following syntheses handling of the perchlorates must be done with caution.¹⁵ Preparations on a larger scale should be avoided. Avoid scraping and (local) heat, and dilute acid mixtures of organic solvents and perchlorate as soon as possible. We did not experience explosions when these precautions were taken.

The syntheses of the perchlorate salts of **1**, **2** and **4** (cf. Scheme 1) were given recently.¹ In the following we describe the syntheses of salts of **3–**, **5+** and of the doubly bridged product (**6+**) derived from **5+** by loss of the non-bridging ammonia molecule. A modification of the synthesis^{5,6} of the ammine analogue of **1** and the synthesis of the ammine analogue of **2+** are also given.

$[(OH) (tacn) Cr(\mu-NH_2)_2 Cr(tacn) (OH)] (ClO_4)_2 \cdot aq$ (**3– salt**). A solution of 100 mg of the perchlorate of **4** (sodium double salt) in 1 ml of 1 M NaOH was heated for 6 min at 95 °C in a water bath (avoid CO₂). The solution was then diluted with 200 ml of cold water and separated on a Sephadex C-25 ion-exchange column with 0.3 M NaClO₄/0.01 M NaOH. The first, red band, containing the cation **3–**, was diluted with water and reabsorbed on a short column of Sephadex C-25 and eluted with 1 M NaClO₄/0.1 M NaOH. After the solution had been concentrated by freeze-drying a red precipitate was formed. It was filtered off, washed with ethanol and diethyl ether and finally air-dried. Yield: a few milligrams of the perchlorate of **3–**.

Some of the starting material, **4**, could be recovered from a second yellow–brownish band from the initial ion-exchange separation.

$[(NH_3) (tacn) Cr(\mu-NH_2) (\mu-OH) Cr(tacn) (OH_2)] (ClO_4)_4$ (**5+ salt**). Ninety milligrams of the perchlorate of **4** (sodium double salt) were dissolved in 0.6 ml of 4 M HClO₄ under stirring. The solution was kept for 30 min at room temperature, then cooled to 5 °C and saturated with LiClO₄. After 20 min a red precipitate was filtered off, washed with ethanol and diethyl ether and finally air-dried. Yield: 37 mg of the perchlorate of **5+** (41%).

$[(H_2O) (tacn) Cr(\mu-NH_2) (\mu-OH) Cr(tacn) (OH_2)] (ClO_4)_4 \cdot 4H_2O$ (**6+ salt**). A solution of 174 mg of the perchlorate of **1** in 1 ml of 1 M HClO₄ was heated for 8.5 min at 95 °C. On cooling the solution in ice water, a red precipitate was formed. After 20 min it was filtered off, washed with ethanol and diethyl ether and finally air-dried. Yield: 90 mg of the perchlorate of **6+** (41%).

$[NH_3]_3Cr(\mu-NH_2)_3Cr(NH_3)_3]Br_3$. (A) An ampoule with 9.3 g of $[Cr(NH_3)_6]Br_3$ was placed in a steel autoclave together with 1.4 g of potassium and 70 ml of liquid ammonia (<20 ppm H₂O). After one day at room temperature the ampoule was broken in the potassium amide solution by shaking the closed autoclave thoroughly. The autoclave was then heated for 3 days at 100 °C. After evaporation of the ammonia the brownish product was dissolved in cold water, filtered and separated by ion-exchange chromatography on Sephadex C-25 using 0.2 M Na₂SO₄ as eluent at 5 °C. First a small red band appeared, followed by a yellow band ($[Cr(NH_3)_6]^{3+}$), and then a brownish one. This band was reabsorbed on a short column of Sephadex C-25 and eluted with 1 M NaBr, and in the eluate $[NH_3]_3Cr(\mu-NH_2)_3Cr(NH_3)_3]Br_3$ crystallized within 1 h at 5 °C. The brown precipitate was filtered off, washed with ethanol and diethyl ether and finally air-dried. Yield: 580 mg (10%).

(B) **Warning!** The following procedure (advantageous because of the high solubility of the starting material in liquid ammonia) has been carried out many times, and no explosions have occurred. However, every precaution

must be taken, because the possibility of an explosion is present.

A mixture of 2 mmol (905 mg) of $[\text{Cr}(\text{NH}_3)_6](\text{ClO}_4)_3$ and 3 mmol of potassium amide in 15 ml of liquid ammonia (dried with sodium) was heated for 3 days at 70 °C in a glass ampoule protected by a metal net. After evaporation of the ammonia, by-products were extracted with two 10-ml portions of cold water. The crude product was suspended in 55 ml of 70 °C water, filtered on 5 g of sodium bromide immediately and quickly cooled to 5 °C. The precipitate was collected on a glass filter, washed with ethanol and diethyl ether and finally air-dried. Yield: 110 mg of $[\text{NH}_3)_3\text{Cr}(\mu\text{-NH}_2)_3\text{Cr}(\text{NH}_3)_3]\text{Br}_3$ (22%).

$[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cr}(\mu\text{-NH}_2)_2\text{Cr}(\text{NH}_3)_4](\text{SO}_4)_4 \cdot 4\text{H}_2\text{O}$. A mixture of 135 mg of $[\text{NH}_3)_3\text{Cr}(\mu\text{-NH}_2)_3\text{Cr}(\text{NH}_3)_3]\text{Br}_3$ and 300 mg of Na_2SO_4 in 5 ml of 0.05 M H_2SO_4 was stirred for 5 min at room temperature. The fine precipitate was collected on a glass filter (G4), washed with water, ethanol and ether and finally air-dried. Yield: 53 mg of $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cr}(\mu\text{-NH}_2)_2\text{Cr}(\text{NH}_3)_4](\text{SO}_4)_4 \cdot 4\text{H}_2\text{O}$ (36%).

Determination of the rate constants. 1 M NaClO_4 was used as medium. As a check, various wavelengths were used for the UV/VIS time drives, but the majority of the results are given for data collected at 266 nm. The sensitivity at this wavelength (Fig. 3) was so high that it was possible to use small amounts of the complex compounds (< 1 mg per experiment) and avoid addition of light-absorbing buffers when $[\text{H}^+]$ or $[\text{OH}^-]$ were larger than 10^{-4} – 10^{-3} M. At intermediate pH it was necessary to use buffers (given elsewhere)¹¹ and, depending on the buffer, to use higher, less sensitive, wavelengths. FPLC data were used as well, especially for the determination of smaller rate constants and as a check of the UV/VIS data.

Some details regarding the determination of the pseudo-first-order rate constants (and equilibrium constants) are given in the following, ordered according to the available reactants (cf. Scheme 1 and the syntheses given above).

Complex 1 (and its ammine analogue). UV/VIS time drives on this complex determined the rate constants for $1 \rightarrow 2+$ and for the corresponding reaction with the ammine analogue. For the ammine analogue some experiments were also performed in 1 M NaBr (this complex is only slightly soluble in 1 M NaClO_4) in order to follow the reaction over as large a pH interval as possible, including the use of buffered solutions. The reactions in 1 M NaClO_4 were followed at 25.0 and 40.0 °C and checked by FPLC. Loss of ammonia plays an increasing role with increasing pH (see below) and for the ammine analogue resulted in unidentified products, including precipitates. Results are given in Fig. 1 and Table 1.

Complex 2. The relatively small rate constants for the disappearance of this complex as a function of pH were

determined mainly by FPLC with control measurements from UV/VIS time drives (including a few measurements at 40 and 55 °C). The products are the species in the lower box of Scheme 1. In basic solution it was also possible to confirm the rate constant for the reaction $3 \rightleftharpoons 4$, and it was here observed that the triply bridged complex is formed prior to the doubly bridged complex. Results are given in Fig. 5.

Complex 3–. An experiment at pH 1 with a salt of this complex was used to check the establishment of the equilibrium between $3+$ and 4 (and the irreversible cleavage of an amido bridge in 4 , see below). Alternatively, we used a solution, rich in $3-$ (containing up to 40–50% of 4), prepared by heating a solution of 4 in 0.1 M NaOH/0.9 M NaClO_4 for 6 min at 95 °C. Most of the data for the $3/4$ system were obtained starting with complex 4 (see below), but in the intermediate pH interval, where the equilibrium is far in favour of 4 , the rate constants could only be determined from the side of the doubly bridged complex. At pH 1 and pH 11–12 the reactions were followed from both sides and showed full agreement.

Complex 4. In acid solution two rate constants could be determined from the UV/VIS time-drive data of this complex: a larger one for the reversible hydroxo-bridge cleavage and one that was up to 100 times smaller for the irreversible cleavage of one amido bridge. The assignment was made on the basis of analogous FPLC experiments. In neutral solution 4 is stable towards hydroxo-bridge cleavage, and in neutral and basic solution inert towards amido-bridge cleavage. Therefore, in basic solution, the time-drive data could be described by only one exponential term, related to the $3/4$ equilibration. The equilibrium ratio, determined from the UV/VIS kinetic data, was confirmed by FPLC data (cf. Fig. 4 and the result at pH 11 mentioned in the Results section). The results of the experiments with 4 and $3-$ (see above) are given in Figs. 1 and 2 and Tables 1 and 2.

Complex 5+. This complex, formed by the irreversible cleavage of one amido bridge in 4 was used for initial studies of the loss of ammonia in analogy with the loss of an ammonia molecule from 2 . The FPLC results obtained, so far, are discussed in the main text.

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