Equilibria between the Hydroxo-Bridged Dinuclear Chromium(III) Complexes with N,N',N''-Trimethyl-1,1,1-tris(aminomethyl)ethane and Their Mononuclear Moieties

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The $[H^+]$-independent dimerization constants, K_D, for the formation of the di- and trihydroxo-bridged dimers $[(H_2O)L_3Cr(OH)_2CrL_3(H_2O)]^{4+}$ (d^{4+}) and $[L_3Cr(OH)_3CrL_3]^{3+}$ (t^{3+}) from their mononuclear moieties have been determined with $L_3 = N,N',N''$-trimethyl-1,1,1-tris(aminomethyl)ethane $(Me_3\text{-tame})$. In 1.0 M NaBr at 25 °C $\log(K_D/M^{-1})$ is $-0.7(1)$ and $5.6(1)$, respectively.

The equilibrium ratio $[d^{3+}]/[t^{3+}]$ with this amine ligand is more than ca. 10^6 times smaller than for the analogue with $L_3 = fac\text{-}(NH_3)_3$, and the rate constant for the first bridge cleavage of t^{3+} is ca. 10^6 times smaller than for the ammonia analogue. The main reason for these differences is probably the steric demands of the $(N^-)CH_3$ group.

Numerous studies in the last decades have thrown light on the equilibria and reactivity of hydroxo-bridged dinuclear metal complexes including their mononuclear moieties, and the subject was discussed in earlier reviews.[1,2] The metal ions have primarily been chromium(III), cobalt(III), rhodium(III) and iridium(III).[3] The role of the trihydroxo-bridged dimer, $[L_3M^{III}(OH)_3M^{III}L_3]^{3+}$, with L_3 being facially coordinated ligands in these octahedral complexes, is especially fascinating. When Wieghardt et al.[4] in 1982 made the first chromium(III) complex of this type it caused a renewed intensity in the study of the reactivity and spectral and magnetic properties of these compounds. Until then rather few trihydroxo-bridged dimers were known, but in the following years several new ones were synthesized and characterized, first of all of chromium(III).

It soon appeared that some of these complexes are remarkably stable and robust in aqueous solution, whereas others undergo bridge cleavage within minutes and can only be synthesized under special conditions.[5] This phenomenon has been connected to the intramolecular steric demands of the ligands.[4] With ligands, L_3, such as N,N',N''-trimethyl-1,4,7-triazacyclononane (metacn) and 1,5,9-triazacyclododecane (tacd) steric hindrance in the dihydroxo-bridged dimers seems to disfavour

these complexes relative to the trihydroxo-bridged ones, which, in contrast, are the less stable when L_3 is $(H_2O)_3$, $(NH_3)_3$ or 1,4,7-triazacyclononane (tacn). The $[(H_2O)_3Cr(OH)_3Cr(H_2O)_3]^{3+}$ ion has never been observed.
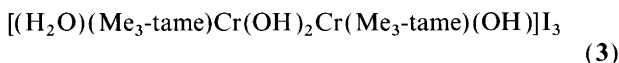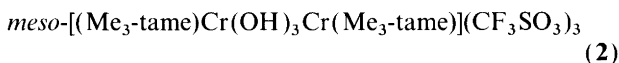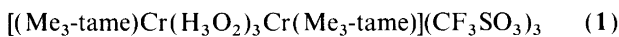
The $[(Me_3\text{-tame})Cr(OH)_3Cr(Me_3\text{-tame})]^{3+}$ ion, where Me_3-tame is N,N',N''-trimethyl-1,1,1-tris(aminomethyl)-ethane, in this respect takes a position between these two extremes. In neutral aqueous solution it is formed within a few hours from the monomer, and in acidic and particularly in basic solution it is cleaved relatively fast to the mononuclear moieties.[6,7] In the following we present equilibrium studies and a few kinetic measurements on this system, which has the unique property that at $4 < \text{pH} < 11$ equilibrium is attained, within reasonable time, from both sides and with measurable amounts of monomer as well as of trihydroxo-bridged dimer. The bridge cleavage of the trihydroxo-bridged dimer in acidic solution was examined, and what we believe is the cis-isomer of the 3+ charged dihydroxo-bridged dimer was isolated.

Results and discussion

Compounds and symbols. Below is given a list of the compounds and symbols, which appear often in the following text.

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Compounds used in the equilibrium and kinetic studies:

$[(Me_3\text{-tame})Cr(H_3O_2)_3Cr(Me_3\text{-tame})](CF_3SO_3)_3$ (1)

meso-$[(Me_3\text{-tame})Cr(OH)_3Cr(Me_3\text{-tame})](CF_3SO_3)_3$
(2)

$[(H_2O)(Me_3\text{-tame})Cr(OH)_2Cr(Me_3\text{-tame})(OH)]I_3$
(3)

Symbols used for this $Cr^{III}(Me_3\text{-tame})$ system:

u: mononuclear species
m: monohydroxo-bridged species
d: dihydroxo-bridged species
t: trihydroxo-bridged species
(a charge is added to the symbol when appropriate)

K_n ($n = 1, 2, ...$): Successive concentration acid dissociation constants (M). K_n is given an extra subscript (u, m, d, t) to specify the species, when necessary. $n = 1$ for u^{3+}, m^{5+}, d^{4+} and t^{4+}, respectively.

K_D: $[H^+]$-independent concentration dimerization constants (M^{-1}):

$$Monomer^{m+} + Monomer^{n+} \rightleftarrows Dimer^{(m+n)+}$$
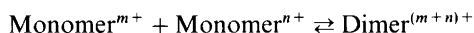
$(m - n$ is 0 or 1)

K_D is given an extra subscript (m, d, t with charge) to specify the dinuclear species.

Isomerism. As pointed out elsewhere[7] coordinated Me_3-tame gives rise to different isomers. The λ, *SSS* (or δ, *RRR*) form seems to be the most stable. λ (or δ) describes the conformation of the $(H_2)C$–N bonds relative to the three-fold axis and S (or R) the configuration around each of the three nitrogen atoms. In Ref. 7, like here, the lone pair at the nitrogen atom has been given the lowest priority in the R,S description. Mixed forms (e.g. λ, *RSS*) have also been isolated in rhodium(III) monomers.[8] In the hydroxo-bridged dimers further isomerism arises from the existence of a *racemic* (λ, *SSS* bridged to λ, *SSS* or δ, *RRR* bridged to δ, *RRR*) as well as a *meso*-form (λ, *SSS* bridged to δ, *RRR*).[7] Furthermore, the dihydroxo-bridged dimer may form a *cis*- and a *trans*-isomer, where *cis* and *trans* refer to the position of the water or non-bridging hydroxide ligands relative to the $Cr(\mu\text{-OH})_2Cr$ plane.

Liquid chromatography (FPLC) of the present equilibrium solutions showed several of these isomers, but the solutions are dominated by the monomer and the trihydroxo-bridged dimer. The FPLC monomer band structure showed major amounts of the λ, *SSS*/δ, *RRR* isomers and a minor, almost constant, fraction of what is supposed to be the mixed forms. The FPLC band of the trihydroxo-bridged dimer contained the *racemic* as well as the *meso*-isomer. At equilibrium they are present in approximately equal concentration as demonstrated also by other methods.[7]

FPLC of the equilibrated solutions showed minor amounts of other species particularly at ca. pH 10. They were not identified with certainty and were not available

in a crystalline state except for an isomer of the dihydroxo-bridged dimer (see later). Some of the bands represent the dihydroxo-bridged dimers, while others contain monohydroxo-bridged dimers. On prolonged standing (months) increasing amounts of other species turned up in the basic solutions at the expense of the mono- and dinuclear complexes. These species are likely to be complexes of higher nuclearity not in equilibrium with the monomer–dimer equilibrium system.

Equilibrium between $[(Me_3\text{-tame})Cr(OH)_3Cr(Me_3\text{-tame})]^{3+}$ and its mononuclear moieties. The contents of mononuclear species and trihydroxo-bridged dimer (sum of the isomers) in the equilibrium solutions in the pH range 4–11 are given in Table 1. Equilibrium was attained from both sides starting with compounds 1 and 2, respectively, described in the beginning of the Experimental section. From the data in Table 1 it is possible to determine the three acid dissociation constants, K_n ($n = 1, 2, 3$), for the monomer $[Cr(Me_3\text{-tame})(H_2O)_3]^{3+}$ (u^{3+}), and the dimerization constant, $K_{D,t^{3+}}$, for the formation of the trihydroxo-bridged dimer (t^{3+}) from the monomers according to the $[H^+]$-independent equilibrium:

$$u^{2+} + u^+ \rightleftarrows t^{3+} + 3H_2O$$
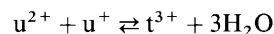
The expression for the determination of these constants is given in eqn. (1):

$$K_{tu} \equiv [t^{3+}] \Big/ \left(\sum_{n=1}^{4} [u^{(4-n)+}] \right)^2$$

$$= K_{D,t^{3+}} K_1^2 K_2 [H^+]^{-3} \Big/$$

$$(1 + K_1[H^+]^{-1} + K_1K_2[H^+]^{-2} + K_1K_2K_3[H^+]^{-3})^2$$

(1)

Least-squares refinements (see Experimental section) using the logarithm of eqn. (1) with $\log(K_{D,t^{3+}}/M^{-1})$ and $pK_n = -\log(K_n/M)$ ($n = 1, 2, 3$) as parameters gave the results shown in Fig. 1.

The three acid dissociation constants were determined[7] also by a fast acid–base titration of the monomer salt 1 (Table 2). The small deviation, almost within the experimental uncertainty, may be caused by the presence of both mononuclear isomers (see above) in the equilibrated solutions, whereas there is only one isomer in the titration experiment. For comparison Table 2 also shows the pK_n values for other *fac*-$[CrL_3(H_2O)_3]^{3+}$ complexes to illustrate the difference, discussed elsewhere,[9] in this respect between the complexes with the inorganic and organic L_3 ligands.

Other metals than chromium form trihydroxo-bridged dimers, but only in the case of cobalt(III) with *cis,cis*-cyclohexane-1,3,5-triamine (tach) has $K_{D,t^{3+}}$ been determined ($10^{9.4}\,M^{-1}$).[10] The magnitude of $K_{D,t^{3+}}$, $10^{5.6}\,M^{-1}$, for this chromium(III) Me_3-tame system cannot be compared directly with that of other chromium(III) systems, since no data exist. Table 2

Table 1. The composition of the equilibrated solutions (3 months in 1.0 M NaBr at 25 °C).[a]

Initial compound	C_{HBr}/M	C_{NaOH}/M	% Cr as t^{3+}	% Cr as u^{n+}	pH_∞	$\log(K_{tu}/M^{-1})$[c]
2	0.0075	0	36.4	58.0	4.47	1.73
1	0.0075	0	28.9	65.9	4.70	1.52
2	0.0050	0	50.1	39.6	4.78	2.20
1	0.0050	0	48.1	43.5	4.89	2.10
2	0.0025	0	73.3	22.3	5.19	2.87
1	0.0025	0	63.4	22.9	5.14	2.78
2	0	0	94.4	trace	6.82	
1	0	0	90.4	trace	6.77	
2	0	0.00125	95.8	trace	7.57	
1	0	0.00125	92.1	trace	7.96	
2	0	0.00167	81.3	8.4	9.21	3.76
1	0	0.00167	72.5	10.3	9.27	3.53
2	0	0.0025	73.9	9.1	9.23	3.65
1	0	0.0025	59.9	15.8	9.45	3.08
2	0	0.0050	24.4	21.5	9.87	2.42
1	0	0.0050	27.5	20.2	9.86	2.53
2	0	0.0100	45.7	22.6	9.99	2.35[b]
1	0	0.0100	43.3	24.8	9.96	2.24[b]
2	0	0.0075	10.4	35.0	10.22	1.62
1	0	0.0075	9.5	31.2	10.22	1.69
2	0	0.0100	6.7	66.0	10.44	0.89
1	0	0.0100	7.0	65.7	10.44	0.91
2	0	0.0125	4.3	89.4	10.72	0.43
1	0	0.0125	4.8	94.7	10.69	0.43

[a]The initial complex was either [(Me₃-tame)Cr(H₃O₂)₃Cr(Me₃-tame)](CF₃SO₃)₃ (**1**) or *meso*-[(Me₃-tame)Cr(OH)₃Cr-(Me₃-tame)](CF₃SO₃)₃ (**2**). [b]C_{Cr} = 0.0100 M except for the solutions with pH_∞ 9.99 and pH_∞ 9.96, where C_{Cr} = 0.0200 M. pH = $-\log([H^+]/M)$. [c]K_{tu} is defined in eqn. (1).

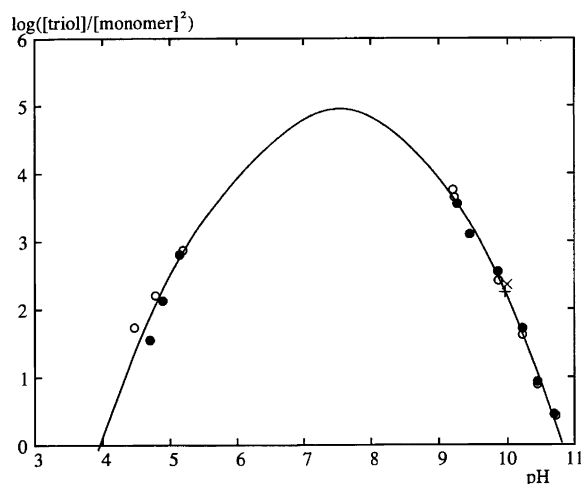$\log([triol]/[monomer]^2)$

Fig. 1. $\log(K_{tu}/M^{-1})$ vs. pH = $-\log([H^+]/M)$ for the equilibrium solutions (1.0 M NaBr at 25 °C). ○ and × denote experiments starting with the dimer and ● and + experiments starting with the monomer. C_{Cr} = 0.0100 M except for the experiments marked with × and +, where C_{Cr} = 0.0200 M. The curve is based on least-squares refinements using eqn. (1) giving the values pK_1 = 4.9(1), pK_2 = 7.5(1), pK_3 = 9.7(1) and $\log(K_{D,t^{3+}}/M^{-1})$ = 5.6(1).

shows a comparison between the dimerization constants of the aqua and the triammine system, where similarities are expected. The resemblance between the variation of the dimerization constants in the two series is remarkable, except for the formation of [(OH)L₃Cr(OH)₂CrL₃(OH)]²⁺ where the difference can

be explained by the formation of an intramolecular H–O⋯H⋯O–H hydrogen bond when L₃ is (H₂O)₃, whereas this is not possible when L₃ is (NH₃)₃.[11,12] In the ammine system [(NH₃)₃Cr(OH)₃(NH₃)₃]³⁺ is hydrolysed completely to the dihydroxo-bridged dimer (from the disappearance of the narrow 332 nm band of the trihydroxo-bridged dimer[5] the higher limit of the equilibrium ratio [t³⁺]/[d³⁺] was determined to be 0.02–0.05). Assuming the $\log K_D$ change (Table 2) on going from the aqua to the ammine series to be close to zero, a rough estimate gives $K_{D,t^{3+}} < 10^4 \, M^{-1}$ for the formation of [(NH₃)₃Cr(OH)₃(NH₃)₃]³⁺.

Kinetic measurements. A simplified model for the reactions in this Me₃-tame system is given in Scheme 1.
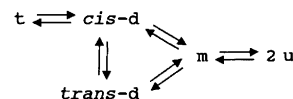
Scheme 1.

However, the reaction scheme is far more complex because of *R,S* and *racemic,meso* isomerization and because of deprotonation of the water ligands and, at extreme pH values, because of protonation or deprotonation of the hydroxo bridges. Only parts of such schemes have been unravelled,[1,5,11,12] and the present Me₃-tame system, where only some of the involved species have been isolated, is no exception from this. Nevertheless, a few simple kinetic measurements,

Table 2. Dimerization constants, K_D [given as $\log(K_D/M^{-1})$], and acid dissociation constants, K_n [given as $pK_n = -\log(K_n/M)$], for *fac*-$[CrL_3(H_2O)_3]^{3+}$ complexes and dimeric derivatives.[a]

L_3:	$(H_2O)_3$[15]	$(NH_3)_3$[5,11,12]	Me_3-tame[b]	tame[18]	tacn[11,14]
Dimerization constants:					
$Cr(OH)Cr^{5+}$ (m^{5+})	−1.2	−1.4	−6.1(3)		
$Cr(OH)Cr^{4+}$	2.1	2.0			
$Cr(OH)Cr^{3+}$	3.9	3.9			
$Cr(OH)Cr^{2+}$		3.0			
$Cr(OH)_2Cr^{4+}$ (*cis,trans*-d^{4+})	3.3	3.5	−0.7(1)		
$Cr(OH)_2Cr^{3+}$	5.7	5.7			
$Cr(OH)_2Cr^{2+}$	5.9	4.5			
$Cr(OH)_3Cr^{3+}$ (t^{3+})		<4	5.6(1)		
Acid dissociation constants:					
Mononuclear species:					
pK_1 (u^{3+})	4.29	5.00	4.78(1)	4.93	4.57
pK_2	6.1	7.27	7.31(1)	7.31	6.74
pK_3		9.28	9.41(1)	9.20	8.85
Monohydroxo-bridged dimers:					
pK_1 (m^{5+})	0.96	1.61			
pK_2	4.30	5.32			
pK_3		8.18			
Dihydroxo-bridged dimers:					
pK_1 (d^{4+}) *trans*	3.68	6.15			5.06
cis		4.09	3.29(2)		2.77
pK_2 *trans*	5.9	7.48			7.24
cis		9.05	9.17(2)		8.84

[a] K_D is the $[H^+]$-independent constant for two mononuclear ions with a charge difference of 0 or 1: $Monomer^{m+} + Monomer^{n+} \rightleftharpoons Dimer^{(m+n)+}$. The log K_D values for the ammine series are relative, i.e. a common constant, probably close to zero, must be added to these values. The medium is 1.0 M $HClO_4$ (1.0 M NaBr for the Me_3-tame series) at 25 °C. The e.s.d., where not quoted in parentheses, can be found in the references, and is ca. 0.1 on log K_D and 0.01–0.1 on pK_n values. [b] This work.

described in the following, have added some pieces of information.

The three available complexes, **1–3** (see Experimental section), were investigated kinetically at 25.0 °C as follows.

d^{3+} *(3) in neutral 1.0 M NaBr.* FPLC showed only two bands, one with d and one with t. The FPLC data could be interpreted as $d^{3+} \rightarrow t^{3+}$ with the rate constant $k_{obs} = 1.03(2) \times 10^{-4}\,s^{-1}$.

d^{3+} *(3) in 0.4 M HBr/0.6 M NaBr.* FPLC showed the same four bands as experiments starting with t^{3+} in the same medium, and the data could be interpreted in accordance with these experiments (see below), i.e. a faster establishment of a pseudo-equilibrium[13] between t^{3+}, d^{4+} and $m^{4+/5+}$ and a slower formation of the final product, u^{3+}.

$u^{+/2+}$ *(1) in neutral 1.0 M NaBr.* FPLC showed the same four bands as above. After 4.5 h ($C_{Cr} = 0.0208$ M) half of the $u^{+/2+}$ was dimerized to approximately equal amounts of d and t (only minor amounts of m). The FPLC data for the first 7 h could be interpreted as $u^{2+} + u^+ \rightarrow$ Dimer with a second-order rate constant equal to $5.8 \times 10^{-3}\,M^{-1}\,s^{-1}$ (seven times smaller than for the aqua system)[15] associated with $d^{3+} \rightarrow t^{3+}$ with

the same rate constant as above. After 48 h t^{3+} accounted for 95% of the chromium content.

t^{3+} *(2) in 0.4 M HBr/0.6 M NaBr.* These experiments will be described in a little more detail. Having compounds **1–3** available the respective concentrations of t, d and u could be determined by FPLC. With our technique we did not observe a splitting of the d-band in a *cis*- and a *trans*-isomer (cf. the first experiment above). One reason may be that this isomerization is relatively fast as shown for other systems,[11] where the rate constant is ca. $10^{-2}\,s^{-1}$. A fourth, relatively small, FPLC band between the u- and the d-band was on basis of the above mentioned experiments interpreted as a m-band, the content of which could only be roughly estimated on the basis of the difference between the total chromium content and the content of t, d, and u.

The cleavage of t^{3+} to u^{3+} was followed by UV/VIS spectrophotometry at selected wavelengths as well as by FPLC separations after quenching. In this acid medium *R,S* isomerization could be neglected, no addition of buffer was needed, and the final product, 100% u^{3+}, was obtained within a day.

Under these conditions the UV/VIS spectral changes as well as the variation of $[t^{3+}]$, $[d^{4+}]$ and $[u^{3+}]$, found

by FPLC, can be described by biexponential expressions[12] with the exponents $n_1 = 0.0034(2)$ s^{-1} and $n_2 = 0.00020(1)$ s^{-1} (least-squares refinements). For the absorbance, A, vs. time, t, the expression is

$$A(t) = (A_0 - A_\infty)\exp(-n_1 t)$$
$$+ A_1[\exp(-n_2 t) - \exp(-n_1 t)] + A_\infty$$

and similar expressions apply to the concentration of the species vs. time. The distribution of the species (FPLC) as a function of time, starting with t^{3+}, is given in Fig. 2, which shows that n_1 approximately describes the initial decrease of [t^{3+}] (also reflected by the course of disappearance of the characteristic sharp spectral t^{3+} peak at 339 nm),[7] while the smaller n_2 approximately describes the slower disappearance of all the dinuclear species, which after 15–30 min have obtained a constant ratio, [t^{3+}]:[d^{4+}]:[$m^{4+/5+}$] = 1:3.4:0.7. According to this, Scheme 1 in this medium can be further simplified as proposed in Scheme 2.

$$t \underset{k_{dt}}{\overset{k_{td}}{\rightleftharpoons}} d \underset{fast}{\overset{K_{dm}}{\rightleftharpoons}} m \overset{k_{mu}}{\longrightarrow} 2\,u$$
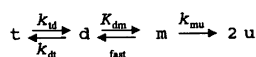
Scheme 2.

With the above mentioned magnitudes for n_1, n_2 and species ratios one gets[13] $k_{td} = 0.0027$ s^{-1}, $k_{dt} = 0.00074$ s^{-1}, $k_{mu} = 0.0015$ s^{-1} and $K_{dm} = 0.19$ ([H$^+$] = 0.4 M). The curves in Fig. 2 are calculated with these values.

From these results the dimerization constant $K_{D,d^{4+}}$ can be calculated: $K_{D,d^{4+}} = K_{D,t^{3+}}K_{2,u}[d^{4+}]/([H^+][t^{3+}]) = 10^{-0.7}$ M^{-1}, i.e. ca. 10^4 times smaller than for the ammonia and water systems (Table 2). $K_{D,d^{3+}}$
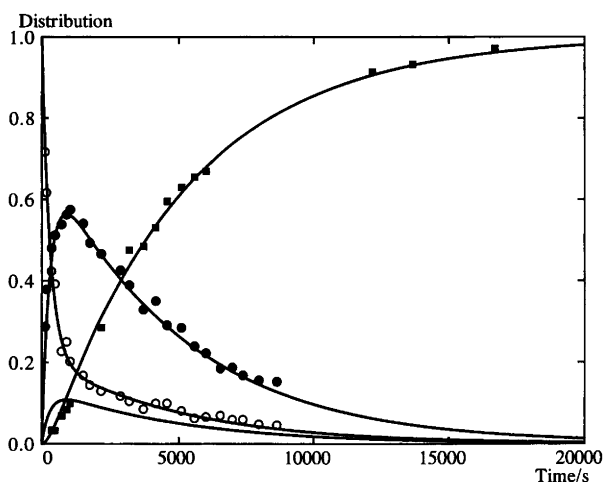

Fig. 2. The distribution of the dinuclear species t^{3+} ($\bigcirc$) and d^{4+} ($\bullet$) and the mononuclear species u^{3+} ($\blacksquare$) vs. time at 25 °C in 0.4 M HBr/0.6 M NaBr. The curves, including the lower curve for $m^{4+/5+}$, are based on Scheme 2 with the values for k_{td}, k_{dt}, k_{mu} and K_{dm} given in the text. The experimental points for $m^{4+/5+}$ are omitted, because no standard was available (see text). However, a maximum was observed around ca. 15 min as expected [$t_{max} = \ln(n_1/n_2)/(n_1 - n_2)$].

$(= K_{D,d^{4+}}K_{1,d}/K_{2,u})$ is ca. 10^3 (depending on the magnitude of $K_{1,d}$) times smaller than $K_{D,t^{3+}}$. This agrees with the absence of $d^{3+/4+}$ in the equilibrated solutions in the pH interval 4–8.

The dimerization constant for m^{5+} can be estimated: $K_{D,m^{3+}} = K_{D,d^{4+}}K_{1,u}[m^{4+/5+}]/\{(K_{1,m} + [H^+])[d^{4+}]\}$ which will be in the interval $10^{-6.1}$–$10^{-5.8}$ M^{-1}, assuming that $K_{1,m}$ is close to or smaller than the value ($10^{-0.5}$ M) for $[(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)]^{5+}$ (en = ethane-1,2-diamine).[1]

[H$^+$] dependence of n_1. The rate of the bridge cleavage of t^{3+} was investigated spectrophotmetrically in the [H$^+$] range 0.1–1.0 M [1.0 M (H,Na)Br at 25.0 °C]. n_1 increases with [H$^+$] due to a dominating pathway via the strong acid, t^{4+}, with an aqua bridge[5] and two hydroxo bridges. The relevant reactions are shown in Scheme 3 (where relatively fast *cis–trans* isomerization of d is assumed[11]).
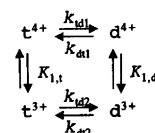
Scheme 3.

With $K_{dt} = k_{dt2}/k_{td2}$ the expression for the rate constant, k_{calc}, is as given in eqn. (2).[11]

$$k_{calc} = (k_{td1}[H^+] + k_{td2}K_{1,t})\{([H^+] + K_{1,t})^{-1}$$
$$+ (1 + K_{1,d}^{-1}[H^+])^{-1}K_{dt}K_{1,t}^{-1}\}$$
$$\approx k_{td1}K_{1,t}^{-1}[H^+] + k_{td1}K_{1,t}^{-1}K_{dt}K_{1,d}$$
$$= k_{td1}K_{1,t}^{-1}[H^+] + k_{dt1} \qquad (2)$$

$$([H^+] \ll K_{1,t}, \; 1 \ll K_{1,d}^{-1}[H^+] \text{ and } k_{td2} \ll k_{td1}K_{1,t}^{-1}[H^+])$$

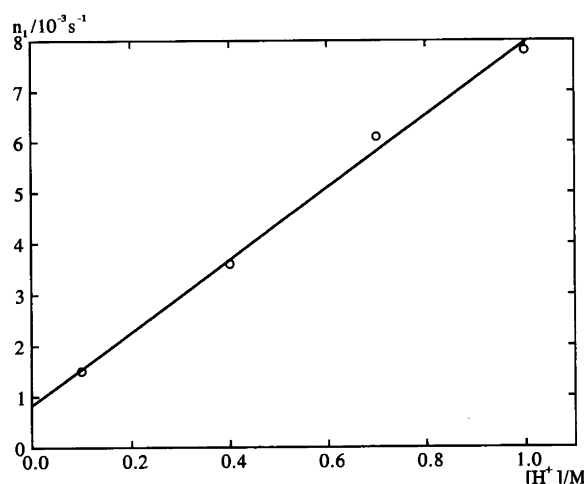The linear relationship between n_1 and [H$^+$] was verified experimentally as shown in Fig. 3, from which

Fig. 3. The rate constant n_1 (*meso*-isomer) vs. [H$^+$] at 25.0 °C in 1.0 M (H,Na)Br. The equation for the line [least-squares refinements using eqn. (2)] is $n_1 = 0.0071(3)[H^+] + 0.0008(2)$ (/s^{-1}).

$k_{dt1} = 0.0008(2)$ s^{-1} and $k_{td1}K_{1,t}^{-1} = 0.0071(3)$ s^{-1} M^{-1}. The magnitude of $k_{td1}K_{1,t}^{-1}$ is ca. 10^6 times smaller than for the ammonia analogue.[5] The value of k_{dt1} agrees with the value $k_{dt} = 0.00074$ s^{-1} found from Scheme 2 by other methods at $[H^+] = 0.4$ M. Agreement is also found using the ratio between k_{dt1} and $k_{td1}K_{1,t}^{-1}$: $K_{D,t^{3+}} / K_{D,d^{4+}} = K_{2,u}^{-1}k_{dt1} / (k_{td1}K_{1,t}^{-1}) = 10^{6.36(12)}$, where the other methods (see above) give $K_{D,t^{3+}}/K_{D,d^{4+}} = [H^+][t^{3+}]/([d^{4+}]K_{2,u}) = 10^{6.38(2)}$. In other words, there is full agreement between the equilibrium ratio $[d^{4+}]/[t^{3+}]$ at $[H^+] = 0.4$ M found from FPLC and found from the $[H^+]$ dependence of n_1 determined by UV/VIS time drives.

In neutral 1.0 M NaBr d^{3+} (3) condenses to t^{3+} with a rate constant $k_{dt} = 1.03 \times 10^{-4}$ s^{-1}. With $K_{D,t^{3+}}/K_{D,d^{3+}} \approx 10^3$ (see above) the rate constant for the reverse bridge cleavage reaction $k_{td} \approx 10^{-7}$ s^{-1}, i.e. 10^5–10^6 times smaller than for the ammine[5] and tacn[14] analogue.

The dihydroxo-bridged dimer. The synthesis of this compound, 3, (see Experimental section) was based on the achieved knowledge of the system according to which 10 min reaction of 2 with 1 M HBr at 25 °C should secure optimum concentration of d^{4+}. After cooling it turned out that it was necessary to deprotonate d^{4+} to get a precipitate. An acetate buffer was used for this purpose. The magnitude of the acid dissociation constants of the dimer gives strong evidence that 3 is the *cis*-isomer (cf. Table 2) and, because of its history, the *meso*-form.

Conclusion

The upper half of Table 2 shows the pronounced difference between the inorganic series with L_3 being $(H_2O)_3$ or $(NH_3)_3$ and the organic series with L_3 being Me_3-tame. Several factors must be considered in a discussion of the magnitudes of the dimerization constants. These factors, some of which are more or less related, are summarized in the following.

Intramolecular hydrogen bonding giving a stabilization of ca. $2 \log K_D$ units for a H–O$\cdots$H$\cdots$O–H bond as demonstrated e.g. in the aqua and ammine series and in the dihydroxo-bridged tacn analogue,[11,12] where such bonds can be established in m^{4+}, m^{3+}, m^{2+} and *cis*-d^{3+} [and apparently also in d^{2+} with $L_3 = (H_2O)_3$].[15]

The number of isomers in the Me_3-tame series has a smaller effect: $\log K_D = 5.6$ (Table 2) covers the sum of the *racemic* and the *meso*-isomer (which at equilibrium are present in approximately equal amounts), and the other K_D values in this series are related to this value. For the *meso*-isomer itself the $\log K_D$ values of this series should therefore be lowered with ca. 0.3.

The increase in charge is probably responsible for the decrease in K_D, most pronounced at high charges.

Steric demands of the ligands, in this case particularly of the $(N^-)CH_3$ group over the nearly planar $Cr(OH)_2Cr$ bridge, is undoubtedly important. Other effects (including solvent effects) are hardly large enough

to explain that the $[t^{3+}]/[d^{3+}]$ equilibrium ratio varies more than a factor 10^5–10^6 from the $(NH_3)_3$ to the Me_3-tame series. The effect is probably even larger with $L_3 = $ metacn,[4] whereas one would expect it to be small with $L_3 = $ tacn, and accordingly the $[t^{3+}]/[d^{3+}]$ ratio with this ligand is found to be less than ca. 10^{-2} (acetonitrile/water mixtures).[14] The steric effect may also be of some importance for the stability of the mono-hydroxo-bridged complexes [e.g. of the type $Cr(\mu\text{-OH})(\mu\text{-H}_3O_2)Cr$]. The steric demands of the ligands, no doubt, also have a considerable influence on the rates of interconversion as demonstrated by the slow bridge cleavage of $[(Me_3\text{-tame})Cr(OH)_3Cr(Me_3\text{-tame})]^{3+}$ in neutral as well as in acidic medium, trihydroxo-bridged dimers with L_3 being metacn[4] or tacd[16] being other examples.

Experimental

Chemicals and complex compounds. The chemicals were of reagent grade or better quality. The mononuclear compound $[(Me_3\text{-tame})Cr(H_3O_2)_3Cr(Me_3\text{-tame})]$-$(CF_3SO_3)_3$ (1) and the dinuclear complex *meso*-$[(Me_3\text{-tame})Cr(OH)_3Cr(Me_3\text{-tame})](CF_3SO_3)_3$ (2) were used as starting materials in the equilibrium and kinetic experiments. They were synthesized as described elsewhere.[6,7] They were analyzed for Cr, C, H and N, and the analyses were within 1–2% in accordance with the given formulae. The synthesis of salts of $[(H_2O)(Me_3\text{-tame})Cr(OH)_2Cr(Me_3\text{-tame})(OH)]^{3+}$ (3), also used in the experiments, is described below.

Apparatus. UV/VIS spectra and time drives were recorded on a Perkin-Elmer Lambda 17 or Lambda 2 spectrophotometer equipped with a thermostat and automatic disk data collection. $[H^+]$ and acid dissociation constants were determined as described elsewhere.[17] The liquid chromatography (FPLC) was performed on a Pharmacia instrument.

Least-squares refinements. Least-squares refinements were based on partial differentiation of the equations, $y = f(x)$, given in the text, where y is $\log K_{tu}$ [eqn. (1)], k_{calc} [eqn. (2)], absorbance (UV/VIS) or species concentration (FPLC). $\Sigma(y_{obs} - y_{calc})^2/w$ was minimized with $w = 1 + \exp(y_{obs} \ln 10)$ when y_{obs} is absorbance and $w = 1$ in the other cases.

Synthesis of the 3+ charged dihydroxo-bridged complex (3). 300 mg of *meso*-$[(Me_3\text{-tame})Cr(OH)_3Cr(Me_3\text{-tame})]Br_3 \cdot 4H_2O$ were dissolved in 6.0 ml of water (25 °C). 2.0 ml of 4.0 M HBr were added, and after 10 min at 25 °C the solution was cooled rapidly to 0 °C. After 5 min at 0 °C 5.44 g (40 mmol) of $Na(CH_3COO) \cdot 3H_2O$ were added, and after a few minutes solid NaI was added until cloudiness (1.0–1.5 g). The mixture (0 °C) was filtered, and further 5 g of NaI were added to the filtrate. After 5–10 min at 0 °C the

precipitate formed was filtered off. The crude precipitate was reprecipitated by dissolution in ca. 2 ml of water at 0 °C, filtration and addition of a little solid NaI. After 5–10 min at 0 °C the precipitate was filtered off and washed with diethyl ether. Yield: 130 mg of the violet iodide of **3** (36% according to Cr analysis).

The perchlorate of **3** (**caution!**)[9] could be obtained from a filtered solution (0 °C) of the iodide (60 mg in 2.5 ml of water) by the addition of 0.75 g of LiClO₄. After 30 min at 0 °C the precipitate was filtered off and washed with a 4:1 mixture of diethyl ether and ethanol, and finally with diethyl ether. Yield: 28 mg of the violet perchlorate of **3** (50% according to Cr analysis).

The crystals of these products were too small for structure analysis by single-crystal X-ray diffraction. FPLC on the products showed that they were contaminated with a little of the trihydroxo-bridged dimer (5–10%), but otherwise behaved as d^{3+} (see Results section). Accordingly a rapid (ca. 10 min) determination of the acid dissociation constants[17] in 1.0 M NaBr at 25 °C showed two constants characteristic for cis-d^{4+}, the presence of the aprote trihydroxo-bridged dimer not disturbing the titration.

FPLC separation of the (Me₃-tame) chromium (III) complexes. With Sephadex SP-C25 ion-exchange resin it was possible to separate the mononuclear species from the complexes of higher nuclearity, whereas these were separated unsatisfactorily. Such separations were used as a model for the much better FPLC with which it was possible to separate the relevant species.

The FPLC used a Mono HR 5/5 column with 2.00 ml injections and UV detection at 254 nm. C_{Cr} in the reacting solutions was 0.01–0.02 M. They were quenched by diluting 50–125 times with 0 °C water or buffer solution of 0.06 M propane-1,3-diamine/0.01 M HBr. When quenched with water an elution gradient from water to 0.02 M amine/0.002 M HClO₄/1.0 M NaCl was used, and when quenched with the amine buffer a gradient from buffer to buffer/1.0 M NaCl was used. In the latter case the amount of mononuclear species could not be determined. This was then done using a buffer of 0.03 M NH₄Cl/0.005 M NH₃ (also as quencher) instead of the amine buffer. The *racemic* and *meso*-isomer of the trihydroxo-bridged could be partly separated using 0.05 M borax as buffer.

Compound **1**, **2** (including the *racemic* isomer)[7] and **3** were used as standards. The species were eluted in the sequence u, m, d and t, the latter after ca. 13 min, and the peak areas over the satisfactorily straight base line were used as a measure for the respective contents of the complexes.

Equilibrium experiments. 1.0 M NaBr was used as inert salt medium, and no complex formation between the chromium complexes and bromide was observed (the solubility of the perchlorate of [(Me₃-tame)-

Cr(OH)₃Cr(Me₃-tame)]³⁺ is too low in 1 M NaClO₄ and chloride coordinates in acidic solutions). Compounds **1** and **2** were used as starting materials in the sealed solutions which were placed at 25 °C for equilibration and followed for up to three months. During the last month of this period the pH and K_{tu} [eqn. (1)] did not change significantly. The composition and final pH of these solutions are given in Table 1.

Kinetic experiments. These experiments and the determination of the rate constants were, in general, performed as described elsewhere.[11,12] As in the equilibrium experiments (see above) the medium was 1.0 M NaBr/HBr at 25.0 °C. Compounds **1–3** were used as reactants, and FPLC (see above) as well as UV/VIS spectrophotometry at 339 nm and other selected wavelengths were used to follow the reactions.

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