

Kinetic Investigations of the *cis*–*trans* Isomerization of Dihydroxo-Bridged Chromium(III) Triamine Dimers with Facially Coordinated Ammonia or 1,4,7-Triazacyclononane

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Dihydroxo-bridged chromium(III) dimers of the type $[(\text{H}_2\text{O})\text{L}_3\text{Cr}(\text{OH})_2\text{CrL}_3(\text{H}_2\text{O})]^{4+}$ exist as *cis*- and a *trans*-isomers with reference to the positions of the two water ligands relative to the $\text{Cr}(\text{OH})_2\text{Cr}$ bridge plane.

The kinetics of the *cis*–*trans* isomerization of such dimers and their deprotonated forms, with L_3 being 1,4,7-triazacyclononane (tacn) or *fac*-(NH_3)₃, was studied spectrophotometrically at $10^{-11} < [\text{H}^+] < 10^{-2}$ M at 25 °C in 1.0 M NaClO_4 . The kinetic data in combination with acid–base titrations allowed the determination of the acid dissociation constants, K_{11} and K_{12} for the *trans*-isomer, K_{c1} and K_{c2} for the *cis*-isomer, and the *cis*/*trans* equilibrium ratios, K_1 , K_2 and K_3 , for the +4, +3 and +2 charged ions, respectively. The experiments demonstrate a direct *cis*–*trans* isomerization path for which the rate constants k_n and k_{-n} ($K_n = k_n/k_{-n}$, $n = 1$ –3) were determined.

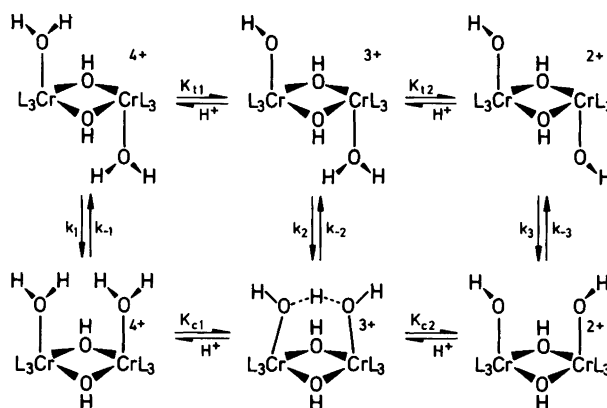
For $\text{L}_3 = \text{tacn}$ ($\text{L}_3 = \text{fac}(\text{NH}_3)_3$ in square brackets) the following values were obtained: $\text{p}K_{11} = 5.06(3)$ [6.15(5)], $\text{p}K_{12} = 7.24(3)$ [7.48(5)], $\text{p}K_{c1} = 2.77(3)$ [4.09(5)], $\text{p}K_{c2} = 8.84(5)$ [9.05(3)], $K_1 = 0.034(3)$ [0.095(15)], $K_2 = 6.7(5)$ [11(2)], $K_3 = 0.17(2)$ [0.29(5)] and $10^4 \times k_{\pm}/\text{s}^{-1}$: k_1 : 4.6(3) [5.8(8)], k_2 : 10.9(5) [6.8(13)], k_3 : 0.9(1), k_{-1} : 136(5) [61(13)], k_{-2} : 1.63(2) [0.62(17)], k_{-3} : 5.1(2).

In the study of the kinetic and thermodynamic properties of hydroxo-bridged complexes with two metal centres the use of metal centres originating from *fac*- $[\text{CrL}_3(\text{H}_2\text{O})_3]^{3+}$ with L_3 being a tridentate amine ligand or $(\text{NH}_3)_3$ has appeared to be advantageous. With these complexes it is possible to investigate the conversion reactions between mono-, di- and trihydroxo-bridged dimers and to do so over a relatively wide $[\text{H}^+]$ range without disturbing polymerization; furthermore, the robustness of the $\text{Cr}^{\text{III}}\text{L}_3$ -moiety facilitates the identification and isolation of the dimers.

The dihydroxo-bridged dimer, $[(\text{H}_2\text{O})\text{L}_3\text{Cr}(\text{OH})_2\text{CrL}_3(\text{H}_2\text{O})]^{4+}$ and its deprotonated forms exist as *trans*- or *cis*-isomers in equilibrium with each other, where *trans* and *cis* refer to the positions of the water and non-bridging hydroxide ligands relative to the $\text{Cr}(\text{OH})_2\text{Cr}$ bridge plane. The enhanced rates of such isomerization reactions have also been observed for dihydroxo-bridged dimers of cobalt(III) and rhodium(III) with various ligands, L_3 .^{1–4} In an earlier paper⁵ we reported the equilibrium constants for the chromium(III) system as determined primarily from acid–base titrations, L_3 being $(\text{NH}_3)_3$ or 1,4,7-triazacyclononane (tacn). The present work deals with the kinetics of this isomerization as followed spectrophotometrically in aqueous solution at room temperature.

Results and discussion

Starting with either the dihydroxo-bridged *cis*-isomer or the *trans*-isomer the *cis*–*trans* isomerization as followed spectrophotometrically (absorbance vs. time) at fixed $[\text{H}^+]$ exhibited first-order kinetics (see Experimental). The reactions involved are given in Scheme 1, for which the expression for the pseudo-first-order rate constant as a function of $[\text{H}^+]$ is given by eqn. (1).



Scheme 1. Reaction scheme for the *cis*–*trans* isomerization of the dimer, showing the symbols used for the rate and equilibrium constants. L_3 is tacn or *fac*-(NH_3)₃. $K_n = k_n/k_{-n}$ ($n = 1$ –3).

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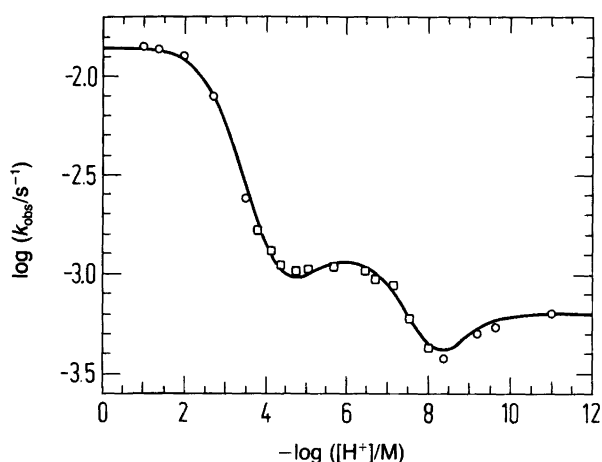


Fig. 1. $\log(k_{\text{obs}}/\text{s}^{-1})$ vs. $-\log([\text{H}^+]/\text{M})$ for the isomerization of the tacn dimer at 25°C in 1.0 M (Na,H)ClO₄. (□) and (○) represent experiments starting with the *trans*- and *cis*-isomer, respectively. The curve is based on eqn. (1) using the constants from Table 1.

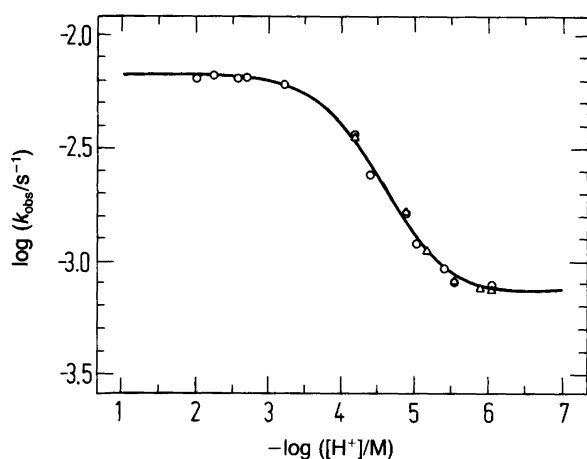


Fig. 2. $\log(k_{\text{obs}}/\text{s}^{-1})$ vs. $-\log([\text{H}^+]/\text{M})$ for the isomerization of the (NH₃)₃ dimer at 25°C in 1.0 M NaClO₄. (Δ) and (○) represent experiments starting with the *trans*- and *cis*-isomer, respectively. The curve is based on eqn. (1) using the constants from Table 1.

$$k_{\text{calc}} = (k_1[\text{H}^+]^2 + k_2K_{11}[\text{H}^+] + k_3K_{11}K_{12})\{([\text{H}^+]^2 + K_{11}[\text{H}^+] + K_{11}K_{12})^{-1} + ([\text{H}^+]^2 + K_{c1}[\text{H}^+] + K_{c1}K_{c2})^{-1}K_1^{-1}\} \quad (1)$$

The $[\text{H}^+]$ -dependence of the observed and calculated pseudo-first-order rate constant is depicted in Figs. 1 and 2, and the deduced rate constants and equilibrium constants are given in Table 1, which includes equilibrium constants originating from earlier acid–base titrations⁵ (see Experimental). As can be seen from Table 1 the loss of ammonia, most pronounced at low $[\text{H}^+]$, is reflected in the higher uncertainties on the constants of the (NH₃)₃ system in comparison with the tacn system, and it was not possible to

Table 1. Rate constants and equilibrium constants for the *cis*–*trans* isomerization (cf. Scheme 1) at 25.0°C in 1.0 M (Na,H)ClO₄ as obtained from kinetic measurements combined with earlier acid–base titrations⁵ (see Experimental).

	L ₃ = tacn	L ₃ = fac-(NH ₃) ₃
$k_1/10^{-4} \text{ s}^{-1}$	4.6(3)	5.8(8)
$k_2/10^{-4} \text{ s}^{-1}$	10.9(5)	6.8(13)
$k_3/10^{-4} \text{ s}^{-1}$	0.9(1)	
$k_{-1}/10^{-4} \text{ s}^{-1 a}$	136(5)	61(13)
$k_{-2}/10^{-4} \text{ s}^{-1 a}$	1.63(2)	0.62(17)
$k_{-3}/10^{-4} \text{ s}^{-1 a}$	5.1(2)	
K_1	0.034(3)	0.095(15)
K_2^b	6.7(5)	11(2)
K_3^b	0.17(2)	0.29(5)
pK_{11}	5.06(3)	6.15(5) ^c
pK_{12}	7.24(3)	7.48(5) ^c
pK_{c1}	2.77(3)	4.09(5)
pK_{c2}	8.84(5)	9.05(3) ^c

^aDerived from $k_{-n} = k_n/K_n$ ($n = 1-3$). ^bDerived from $K_{n+1} = K_nK_{cn}/K_n$ ($n = 1-2$). ^cFrom Ref. 5.

obtain reliable kinetic data for the (NH₃)₃ system at $[\text{H}^+] < 10^{-7}$ M. Otherwise the tacn and the (NH₃)₃ systems behave rather similarly, and are treated together in the following discussion.

The equilibrium constants of Table 1 demonstrate the relatively high stability of the +3 charged *cis*-dimer. The reason for this stability is that this dimer forms a strong intramolecular H–O---H---O–H hydrogen bond between the non-bridging hydroxide and water ligands as indicated in Scheme 1. The existence of such a bond and its significance for the high stability of this and similar dimers are well documented and discussed elsewhere.⁵⁻⁹ In the present case it is possible to estimate the ratio, K_H , between the equilibrium concentrations of this *cis*-dimer and the corresponding +3 charged *cis*-dimer without such a hydrogen bond, as well as the corresponding stability, K'_H , of an intramolecular H–O---H–O hydrogen bond in the +2 charged *cis*-isomer. With K'_{c1} and K'_{c2} being the acid dissociation constants of the *cis*-isomer forming no hydrogen bonds $K_{c1} = K'_{c1}(1 + K_H)$ and $K_{c2} = K'_{c2}(1 + K'_H)/(1 + K_H)$. In estimates of K_H for these and for monohydroxo-bridged tetraamine dimers Springborg⁶ suggests the approximation that $K'_{c1}/K'_{c2} \approx K_{11}/K_{12}$ and $K'_H \approx 0$, resulting in $K_H \approx [K_{c1}K_{12}/(K_{c2}K_{11})]^{1/2} - 1$. In the present case an alternative is to use the approximation that $K'_{c1} \approx K_{11}$ and $K'_{c2} \approx K_{12}$, resulting in $K_H \approx (K_{c1}/K_{11}) - 1$ and $K'_H \approx [K_{c1}K_{c2}/(K_{11}K_{12})] - 1$. With this approximation $\log K_H$ is 2.3 (tacn) and 2.1 [(NH₃)₃], while $\log K'_H$ is only 0.6 (tacn) and 0.3 [(NH₃)₃].

The order of the rate constants is $k_{-1} > k_2 > k_1 > k_{-2}$ for both the tacn and the (NH₃)₃ systems. There is a tendency for the (NH₃)₃ system to show slower isomerization than the system with the organic ligands. A similar difference in reactivity has been observed⁶ for the conversion between mono- and dihydroxo-bridged chromium(III) dimers with four ammonia or two 1,2-ethanediamine ligands on each chromium centre.

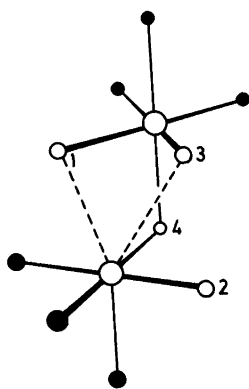


Fig. 3. The idealized transition-state structure suggested by Mønsted *et al.*⁹ for the bridge shift mechanism in dihydroxo-bridged species.

The following discussion of the relative magnitudes of the rate constants is limited to k_1 , k_2 and k_3 . As $k_{-n} = k_n/K_n$ ($n = 1-3$) the relative magnitudes of the reverse rate constants can be related to k_n through the discussion of the K_n -values given above. Mønsted *et al.*⁹ have suggested a bridge shift mechanism for dihydroxo-bridged species which involves a transition state, the idealized structure of which is shown in Fig. 3. Using this model for the k_n situation, i.e. with O3 and O4 as the original bridge oxygen atoms, it is likely that increased rates are obtained when there is a possibility for the O3 hydroxide bridge to become more water-like by means of a nearby hydrogen atom (H^*) participating in a $H-O3---H^*-O-H$ intramolecular arrangement. This is not possible in the +2 charged case, and in accordance with this k_3 (tacn) is significantly smaller, approximately an order of magnitude, than k_1 and k_2 . In the +3 and +4 charged ions H^* may be placed either in the region between O1 and O3 or between O2 and O3, and in the +4 charged case a proton has to be removed from O1, and O3 must receive one. However, the small difference between k_1 and k_2 , not significant for the $(NH_3)_3$ system, can hardly be rationalized, especially as we have not been able to produce reliable activation parameters so far. In favour of a small k_1 relative to k_2 speaks the labilizing effect of OH^- compared to H_2O (O2) if H^* is in the O1-O3 region; if H^* is in the O2-O3 region no proton need be removed from O1 in the +3 charged ion, and in addition one might expect coordinated OH^- to be a better nucleophile than coordinated H_2O (O1).

The results and discussion above are based on the model of Scheme 1 with a direct pathway between the equally charged isomers. An obvious alternative might be a mechanism via the monohydroxo-bridged dimers. Actually the rate constants for bridge cleavage and formation of dihydroxo- and monohydroxo-bridged chromium(III) dimers, respectively, with four ammonia or two 1,2-ethanediamine ligands on each chromium centre,⁶ are in the range 10^{-4} – 10^{-2} s⁻¹, i.e. the same range as for the present isomerization reactions. For the $(NH_3)_3$ system it has been possible to isolate the monohydroxo-bridged dimer. The equi-

librium ratio between the mono- and dihydroxo-bridged dimers (*cis* plus *trans*) is 0.02–0.03 at $10^{-7} < [H^+] < 10^{-2}$ M (+2 to +4 charged species). Kinetic measurements of the condensation of the mono- to the dihydroxo-bridged dimers in this $[H^+]$ interval show that bridge cleavage of the +4 charged *cis*-isomer is 40 times slower than isomerization to the *trans*-isomer (k_{-1}), and that bridge cleavage of the +3 charged *trans*-isomer is 3–4 times slower than isomerization to the *cis*-isomer (k_2). From kinetic measurements of the condensation at $10^{-6} < [H^+] < 10^{-4}$ M it was possible in one experiment to observe two different rates, one for isomerization in accordance with that found from the present direct isomerization experiments, and another for bridge cleavage/formation. Thus, within the experimental uncertainty the present values of $k_{\pm 1}$ and $k_{\pm 2}$ [$(NH_3)_3$] are not influenced by a pathway via the monohydroxo-bridged dimer. This is probably also true for the isomerization rate constants of the tacn system, where it has not been possible to isolate the monohydroxo-bridged species or to detect them in solution. A more detailed report on the kinetic behaviour of the mono- and trihydroxo-bridged dimers of the $(NH_3)_3$ system is in preparation.¹⁰

The *cis*–*trans* isomerization has also been studied for cobalt(III) [and briefly for rhodium(III)] in connection with bridge cleavage of trihydroxo-bridged dimers with various amine ligands.¹⁻⁴ As in the chromium case, $K_1 < 1$ [0.035 for cobalt(III) with $L_3 = (NH_3)_3$].¹ k_1 and k_{-1} are, however, greater than the values for the chromium(III) case [0.0066 s⁻¹ and 0.186 s⁻¹, respectively, for the triamminecobalt(III) system].¹ A more detailed discussion can be seen elsewhere.⁶

Experimental

Chemicals and complex compounds. The chemicals were of reagent grade or of a similar or (for the kinetic measurements) better quality. The chromium(III) dimers were synthesized as described elsewhere.⁵ It should be noticed that in this reference a perchlorate of a +3 charged dimer was erroneously assigned as a dihydroxo-bridged *cis*-isomer. As shown later¹¹ it is actually a salt of the trihydroxo-bridged dimer, $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3]^{3+}$, which in aqueous solution reacts to give the dihydroxo-bridged *cis*-dimer at a rate comparable to the rate of dissolution. The compounds used for the kinetic measurements were, besides this salt, *trans*- $[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH)](ClO_4)_3 \cdot H_2O$, *trans*- $[(OH)(tacn)Cr(OH)_2Cr(tacn)(OH)](ClO_4)_2 \cdot 1.5 H_2O$, and *cis*- $[(H_2O)(tacn)Cr(OH)_2Cr(tacn)(OH)]I_3 \cdot 3 H_2O$. Spectral data (UV/VIS) for the ammonia complexes are given in Refs. 11 and 12, and the tacn complexes have similar spectra.

Apparatus. Visible absorption spectra and time drives at fixed wavelengths were measured on a Cary 118 or a Perkin-Elmer Lambda 17 spectrophotometer with thermostatted cell-holders. $[H^+]$ was measured on a Radiometer PHM 52 instrument as described elsewhere.⁵

Table 2. Applied buffers with specification of $-\log ([H^+]/M)$ range at 25°C in 1.0 M NaClO₄.

2-methylpyrazine	2.0–2.3	3-methylpyridine	6.0–6.3
pyridazine	2.5–2.8	2,6-dimethylpyridine	6.8–7.0
sulfanilic acid	3.0–3.2	1,2-ethanediamine	7.2–7.6
2-pyrimidineamine	3.7–4.1	1,5,9-triazanonane	8.0–8.3
2-pyridinesulfonic acid	4.4–4.6	1,3-propanediamine	9.0–9.3
aniline	4.8–5.1	1,4-butanediamine	9.6–9.9
pyridine	5.5–5.7	1,3-propanediamine	10.5–10.7
		1,4-butanediamine	10.9–11.1

Determination of the observed rate constants. All measurements were performed at 25.0°C in 1.0 M (Na,H)ClO₄. Table 2 lists the buffers used in the $[H^+]$ -range 10^{-11} – 10^{-2} M with a buffer concentration of 0.03–0.05 M and a chromium dimer concentration 10 times as small. The salt of the dimer was weighed into a 1 cm cell, 3.00 ml of thermostatted buffer solution were added, and stirring was maintained in the cell placed in the thermostatted cell-holder. The reactions were followed for 7–8 half-lives, and $[H^+]$ of the buffer solutions and of the reacted solutions was measured, showing pH-changes during the reaction of, at most, 0.05 pH-units.

From the absorbance (A) vs. time (t) data the observed pseudo-first-order rate constants, k_{obs} , were calculated by least-squares refinement to eqn. (2), where the last term

$$A(t)_{obs} = (A_0 - A_\infty) \exp(-k_{obs}t) + A_\infty + \alpha t \quad (2)$$

makes allowance for a small linear correction due to the loss of ammonia at $[H^+] < ca. 10^{-5}$ M. At 7 half-lives αt was at most 2–3 % of $A_0 - A_\infty$, and at a given wavelength α was roughly proportional to the chromium concentration. Some of the added buffers exhibited absorbance below ca. 450 nm, but by choosing fixed wavelengths between 500 and 650 nm this was not a problem.

Under these circumstances good fits to eqn. (2) were obtained, and as a control the following matters were checked for some of the experiments: (i) Measurements at different wavelengths at the same $[H^+]$ gave the same k_{obs} . (ii) Moderate changes of the chromium or the buffer concentration did not affect k_{obs} . (iii) There was no spectral indication of reactions between the buffers and the dimers under the described experimental conditions. Two different buffers at the same $[H^+]$ gave the same k_{obs} . At $[H^+] > 10^{-2}$ M solutions without buffer were used. A few less accurate pH-stat measurements at $[H^+] \approx 10^{-4}$ M gave the same k_{obs} as the buffer experiments. Within the experimental uncertainty the same k_{obs} value was obtained

whether the experiment was started with the *trans*- or the *cis*-dimer, and the final equilibrium ratio, $[cis-dimer]/[trans-dimer]$, agreed with that found from earlier equilibrium measurements⁵ on solutions without added buffer. (iv) No HCO_3^-/CO_3^{2-} interference was observed.

The rate constants and the equilibrium constants. The expression for the pseudo-first-order rate constants as a function of $[H^+]$ is given in eqn. (1). In the least-squares refinement to this expression for the tacn system all the constants k_1 , k_2 , k_3 , K_{t1} , K_{t2} , K_{c1} , K_{c2} and K_1 were included as parameters. Also included, with the same weight as the kinetic experiments, was the variance matrix from the previous determination of the last five constants from acid–base titrations.⁵ The same procedure was used for the $(NH_3)_3$ system where, however, only k_1 , k_2 , K_{c1} and K_1 were included as parameters in the refinements.

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References

- Jentsch, W., Schmidt, W., Sykes, A. G. and Wieghardt, K. *Inorg. Chem.* 16 (1977) 1935.
- Wieghardt, K., Schmidt, W., Nuber, B. and Weiss, J. *Chem. Ber.* 112 (1979) 2220.
- Wieghardt, K., Schmidt, W., van Eldik, R., Nuber, B. and Weiss, J. *Inorg. Chem.* 19 (1980) 2922.
- Wieghardt, K., Schmidt, W., Nuber, B., Prikner, B. and Weiss, J. *Chem. Ber.* 113 (1980) 36.
- Andersen, P., Døssing, A. and Nielsen, K. M. *Acta Chem. Scand., Ser. A* 40 (1986) 142.
- Springborg, J. In: Sykes, A. G., Ed., *Advances in Inorganic Chemistry*, Academic Press, New York 1988, Vol. 33, p. 47 and references therein.
- Andersen, P. In: Lever, A. B. P., Ed., *Coordination Chemistry Reviews*, Elsevier, Amsterdam 1989, Vol. 94, p. 47 and references therein.
- Andersen, P., Døssing, A. and Larsen, S. *Acta Chem. Scand.* 44 (1990) 455.
- Mønsted, L., Mønsted, O. and Springborg, J. *Inorg. Chem.* 24 (1985) 3496.
- Andersen, P. and Døssing, A. *To be published.*
- Andersen, P., Døssing, A., Larsen, S. and Pedersen, E. *Acta Chem. Scand., Ser. A* 41 (1987) 381.
- Andersen, P., Nielsen, K. M. and Petersen, A. *Acta Chem. Scand., Ser. A* 38 (1984) 593.

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