Thermal and Photochemical Hydrolysis and Water Exchange Reactions of Aqua(1,3-propanediamine) Complexes of Chromium(III)

L. Mønsted[a,*] and O. Mønsted[b]

[a]Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg C and [b] Department of Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 København Ø, Denmark

Mønsted, L. and Mønsted, O., 1993. Thermal and Photochemical Hydrolysis and Water Exchange Reactions of Aqua(1,3-propanediamine) Complexes of Chromium(III). – Acta Chem. Scand. 47: 9–17.

The thermal and photochemical reactivity of aqua(1,3-propanediamine)-chromium(III) complexes, including amine ligand aquation, isomerization and water ligand exchange, has been investigated using an acidic 1 M perchlorate medium.

The amine ligand aquation reactions are characterized by significant reactivity differences between the dechelation reaction and the following aquation reaction of the protonated monodentate amine. Species with the latter ligand being coordinated have not been observed in appreciable amounts. This reactivity difference is even more pronounced for the photochemical reactions than for the thermal reactions.

The thermal water ligand exchange reactions are dominated by stereoretentive reactivity contributions, but the significant robustness of the chelate diamine ligand results in greater reactivity contributions from isomerization reactions than are normally observed for thermal reactions of amineaquachromium(III) complexes. The photochemical reactions are dominated by isomerization reactions accompanied by exchange of coordinated water.

Differences in product distribution ratios between competing thermal and competing photochemical reactions can be accounted for in terms of differences in the enthalpies of activation for the processes. The comparative thermal and photochemical reactivity studies are indicative of significant similarities in the energy contributions for the metal–ligand bond-breaking reactions in the electronic ground state and in the more reactive excited states.

In spite of the dominating role of aqueous media in the study of the photochemical reactivity of transition metal complexes, and the facile coordination of solvent water in such complexes, few studies on photoinduced water ligand exchange reactions have appeared.

The ammineaquachromium(III) complexes probably constitute the most complete series of complexes for which photoinduced water ligand exchange reactions have been characterized.[1] These studies have provided the experimental background for the suggestion of the operation of a solvent-assisted excited state deactivation process in these systems.

Key experiments in this research have been the study of reactions for which both thermal and photochemical pathways are available. Few systems are suitable for such studies from an experimental point of view,[1] but selected 1,3-propanediamine complexes of chromium(III) might provide an opportunity to extend the earlier studies to include a larger number of leaving ligands, including also the cationic 3-aminopropyl-1-ammonium ligand. Abbreviations for ligand names are given in Table 1.

Results and discussion

Thermal reactivity of cis- and trans-$[Cr(tn)_2(OH_2)_2]^{3+}$: Ion-exchange chromatography on thermally hydrolyzed solutions of cis- and trans-$[Cr(tn)_2(OH_2)_2]^{3+}$ in acidic solutions allows the isolation of minor amounts of 4+ charged species. The eluate of 4+ charged species obtained by ageing the cis-$[Cr(tn)_2(OH_2)_2]^{3+}$ complex

Table 1. Ligand name abbreviations.

tn	1,3-Propanediamine
m-tn	Monodentate 1,3-propanediamine
tnH	3-Aminopropyl-1-ammonium ion
en	1,2-Ethanediamine
am, am'	Amine ligands
aq	Water

---

* To whom correspondence should be addressed.
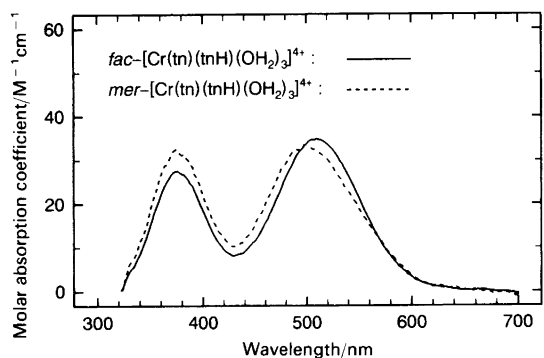
Fig. 1. Visible absorption spectra of the isomeric [Cr(tn)(tnH)(OH₂)₃]⁴⁺ complexes in 0.1 M HClO₄ + 0.9 M NaClO₄.

for 1 to 2 half lives can be separated into fractions with different visible absorption spectra, as shown in Fig. 1. Hydrolyzed solutions of the *trans* isomer contain significantly smaller amounts of 4+ charged species, and well defined fractionation experiments could not be performed. The visible absorption spectrum of the undivided 4+ charged eluate, however, is similar to the first fraction of the 4+ charged eluate from the hydrolyzed *cis* complex. Spectral and reactivity comparisons with the analogous ammineaquachromium(III) complexes[2] and aqua(1,2-ethanediamine)chromium(III) complexes[3] make it likely that the eluates of 4+ charged species contain the isomeric [Cr(tn)(tnH)(OH₂)₃]⁴⁺ complexes. Apparently the *cis*-tetraamine complex gives both the *mer* and *fac* triamine isomers, whereas the *trans*-tetraamine only reacts to give the *mer* triamine complex. From the fractionation experiments it is apparent that significantly larger quanties of the *fac* triamine isomer than of the *mer* isomer are present in hydrolyzed solutions of the *cis*-tetraaminediaquachromium(III) ion. If the reactivity comparisons with the ammonia complexes[2] are valid, this may be the result of a combined effect of a higher

formation rate and a lower rate for the following aquation reaction of the *fac vs.* the *mer* triamine isomer.

Eluates of 3+ charged species obtained from aged solutions of *cis*-[Cr(tn)₂(OH₂)₂]³⁺ are mixtures dominated by the parent tetraamine isomer and the [Cr(tn)(OH₂)₄]³⁺ complex. Eluates of aged solutions of the *trans* isomer, however, are found to contain significant amounts of both the *cis* and the parent *trans* tetraamine isomer in addition to the diamine complex. This establishes the stoichiometry of the reactions given in Scheme 1. At longer reaction times [Cr(tnH)(OH₂)₅]⁴⁺ and [Cr(OH₂)₆]³⁺ are formed from [Cr(tn)(OH₂)₄]³⁺ as previously described.[4]
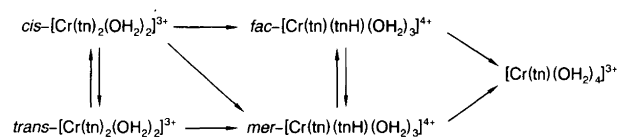
Scheme 1.

Kinetic experiments were carried out at a series of temperatures between 55 and 75°C using an acidic 1 M perchlorate medium. The reactions were followed spectrophotometrically on thermally quenched reaction mixtures by spectral measurements from 300 to 700 nm. The data were interpreted within the stoichiometry of Scheme 1. The limited amount of the *mer* triamine complex did not, however, allow the extraction of meaningful kinetic parameters for the reactivity of this complex from the present type of measurements. Furthermore, it was not possible to determine the interconversion rates for these triamine complexes and the relative formation rates from the tetraamine complexes when the stoichiometric reaction scheme was supplemented with the triamine isomerization reactions. From the stoichiometric experiments it appears likely that only the *mer* triamine is formed directly from the *trans* tetraamine. The final calculations

Table 2. Rate constants at 70°C and activation parameters for amine ligand aquation and isomerization of aqua(1,3-propanediamine)chromium(III) complexes in 0.5 M HClO₄ + 0.5 M NaClO₄ (standard deviations in parenthesis).

Reactant	Product	$10^6 k(70°C)/s^{-1}$	$\Delta H^*/kJ\ mol^{-1}$	$\Delta S^*/J\ K^{-1}\ mol^{-1}$
[Cr(tn)₃]³⁺	*cis*-[Cr(tn)₂(tnH)(OH₂)]⁴⁺	7.57(12)	110(2)	−25(6)
cis-[Cr(tn)₂(tnH)(OH₂)]⁴⁺	*cis*-[Cr(tn)₂(OH₂)₂]³⁺	85(10)		
	?-[Cr(tn)(tnH)₂(OH₂)₂]⁵⁺	12.7(13)		
trans-[Cr(tn)₂(tnH)(OH₂)]⁴⁺	*trans*-[Cr(tn)₂(OH₂)₂]³⁺	18(4)		
	cis-[Cr(tn)₂(OH₂)₂]³⁺	11(5)		
	?-[Cr(tn)(tnH)₂(OH₂)₂]⁵⁺	5.1(15)		
cis-[Cr(tn)₂(OH₂)₂]³⁺	*trans*-[Cr(tn)₂(OH₂)₂]³⁺	1.5(3)		
	fac-[Cr(tn)(tnH)(OH₂)₃]⁴⁺	5.4(10)		
	mer-[Cr(tn)(tnH)(OH₂)₃]⁴⁺	0.0(5)		
trans-[Cr(tn)₂(OH₂)₂]³⁺	*cis*-[Cr(tn)₂(OH₂)₂]³⁺	6.6(2)	142(6)	69(20)
	mer-[Cr(tn)(tnH)(OH₂)₃]⁴⁺	5.6(2)	105(6)	−40(20)
fac-[Cr(tn)(tnH)(OH₂)₃]⁴⁺	[Cr(tn)(OH₂)₄]³⁺	9(3)		
[Cr(tn)(OH₂)₄]³⁺	[Cr(tnH)(OH₂)₅]⁴⁺	0.650(7)ᵃ	105.5(13)	−57(4)
[Cr(tnH)(OH₂)₅]⁴⁺	[Cr(OH₂)₆]³⁺	0.66(2)ᵃ	121(4)	−11(13)

ᵃ Data from Ref. 4.

Table 3. Rate constants at 25°C and activation parameters for the exchange of *one* water ligand in some tetraaminedia-quachromium(III) complexes (standard deviations in parenthesis).[a]

Complex	$10^6 k(25°C)/s^{-1}$	$\Delta H^*/kJ \, mol^{-1}$	$\Delta S^*/J \, K^{-1} \, mol^{-1}$
cis-$[Cr(tn)_2(OH_2)_2]^{3+}$	35.4(4)	101.2(12)	9(4)
cis-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	59.2(13)	95.1(19)	−7(6)
trans-$[Cr(tn)_2(OH_2)_2]^{3+}$	10.0(2)	98.6(12)	−10(4)
trans-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	11.7(3)	98.5(21)	−9(7)

[a] Data for the ammonia complexes are from Ref. 5.

were performed by neglecting the *mer* triamine concentration from the rate expressions, i.e. assuming direct formation of the diaminetetraaquachromium(III) complex from the tetraaminediaquachromium(III) isomers. The triamine isomerization reactions and the direct formation of the *fac* triamine isomer from the *trans* tetraamine isomer were not taken into account. This latter process would require an extensive stereochemical rearrangement, and evidence for such a type of reaction has apparently never been obtained for a chromium(III) complex. The kinetic parameters are given in Table 2.

The water exchange reactions were followed mass spectrometrically on the solvent water using oxygen-18 labelled *cis*- and *trans*-$[Cr(tn)_2(OH_2)_2]^{3+}$ in an acidic 1 M perchlorate medium. The kinetic parameters in Table 3 have been obtained from a series of kinetic experiments covering the temperature range 15–45°C.

Photochemical reactivity of cis- and trans-$[Cr(tn)_2(OH_2)_2]^{3+}$ complexes. Solutions of *cis*- and *trans*-$[Cr(tn)_2(OH_2)_2]^{3+}$ were irradiated at 366 nm in an acidic 1 M perchlorate medium at 25°C. Ion-exchange chromatography revealed a significant isomerization between the tetraamine isomers but showed only minor amounts of the $[Cr(tn)(OH_2)_4]^{3+}$ complex. 4+ charged complexes with monodentate protonated amine ligand did not appear in sufficient quantities for a spectral identification, and even several hours of irradiation did not produce measurable amounts of $[Cr(OH_2)_6]^{3+}$. The photochemical data were interpreted within the stoichiometry of Scheme 2. The quantum yields are given in Table 4.
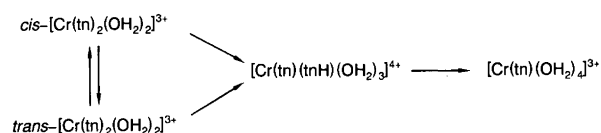
Scheme 2.

Photochemical water exchange of the two tetraamine complexes was measured in a 1 M perchlorate medium at 25°C by irradiation at 366 and 546 nm, respectively, cf. Fig. 3.The quantum yields obtained on the basis that the isomerization reactions are accompanied by exchange of coordinated water are given in Table 4.

Thermal and photochemical reactivity of $[Cr(tn)_3]^{3+}$ and of the isomeric $[Cr(tn)_2(tnH)(OH_2)]^{4+}$ complexes. Ion-exchange chromatography of thermally hydrolyzed solutions of $[Cr(tn)_3]^{3+}$ shows minor amounts of 4+ and 5+ charged species. The visible absorption spectra of fractions of the eluate of 4+ charged species are identical at smaller degrees of conversion of the hexaamine complex, and an apparently pure species can be isolated by such fractionation experiments. The spectral properties in acidic and basic solutions are indicative of pentaamina-qua- and pentaaminehydroxochromium(III), respectively, cf. Fig. 2. The isolated species can be titrated as a divalent acid, cf. the data in Table 5, and it reacts to give only *cis*-$[Cr(tn)_2(OH_2)_2]^{3+}$ as the first 3+ charged reaction product. The thermally produced species is therefore assumed to be the *cis*-$[Cr(tn)_2(tnH)(OH_2)]^{4+}$ complex, with *cis* referring to the relative position of the water and the 3-aminopropyl-1-ammonium ligand.

Table 4. Amine ligand photosubstitution and photoisomerization quantum yields for aqua(1,3-propanediamine)-chromium(III) complexes in 0.5 M $HClO_4$ + 0.5 M $NaClO_4$ at 25°C irradiated at 366 nm (standard deviations in parenthesis).

Reactant	Product	$\phi/mol \, einstein^{-1}$
$[Cr(tn)_3]^{3+}$	?-$[Cr(tn)_2(tnH)(OH_2)]^{4+}$	0.206(5)
cis-$[Cr(tn)_2(tnH)(OH_2)]^{4+}$	?	0.29(8)
trans-$[Cr(tn)_2(tnH)(OH_2)]^{4+}$	?	0.25(7)
cis-$[Cr(tn)_2(OH_2)_2]^{3+}$	*cis*-$[Cr(tn)_2(OH_2)_2]^{3+}$	0.030(6)[a]
	trans-$[Cr(tn)_2(OH_2)_2]^{3+}$	0.202(9)
	?-$[Cr(tn)(OH_2)_3]^{4+}$	0.006(2)
trans-$[Cr(tn)_2(OH_2)_2]^{3+}$	*trans*-$[Cr(tn)_2(OH_2)_2]^{3+}$	−0.009(8)[a]
	cis-$[Cr(tn)_2(OH_2)_2]^{3+}$	0.368(13)
	?-$[Cr(tn)(tnH)(OH_2)_3]^{4+}$	0.009(4)

[a] These quantum yields are calculated assuming that isomerization is accompanied by water ligand exchange.

Fig. 2. Visible absorption spectra of the isomeric $[Cr(tn)_2(tnH)(OH_2)]^{4+}$ complexes in 1 M $(Na,H)(ClO_4,OH)$. Spectra of the aquapentaamine complexes are measured in solutions with $[H^+] \approx 0.1$ M and the spectrum of the deprotonated complex in a solution with $[OH^-] \approx 0.1$ M.

Ion-exchange chromatography on photolyzed solutions of $[Cr(tn)_3]^{3+}$ shows an elution pattern similar to that of the thermally hydrolyzed solutions. Small amounts of both 4+ and 5+ charged species are seen, but in contrast to the behaviour of the thermally hydrolyzed solutions, visible absorption spectra of the fractions of the eluate of 4+ charged species are not identical. Thermal hydrolysis of a purified solution of this eluate gives mixtures of cis- and trans-$[Cr(tn)_2(OH_2)_2]^{3+}$ as the first reaction products. The eluate of 4+ charged species from photolyzed solutions of the hexaamine complex is therefore assumed to contain a mixture of the cis- and trans-$[Cr(tn)_2(tnH)(OH_2)]^{4+}$ isomers. Sufficient quantities, however, were never accessible for a quantitative macroscopic separation, although the relative cis/trans content of the eluates of 4+ charged species could be determined by FPLC chromatography. This provided the analytical basis for the calculation of the spectrum of the pure trans pentaamine isomer given in Fig. 2.

Eluates of the 5+ charged species from both the thermal and photochemical experiments were too dilute to give reproducible visible absorption spectra. The pink colour on the ion-exchange resin, however, might accord with a mixture of $[Cr(tn)(tnH)_2(OH_2)_2]^{5+}$ isomers.

The thermal hydrolysis of $[Cr(tn)_3]^{3+}$, of cis-

$[Cr(tn)_2(tnH)(OH_2)]^{4+}$ and of the cis/trans-$[Cr(tn)_2(tnH)(OH_2)]^{4+}$ mixture were followed at a series of temperatures between 55 and 75°C. These data, in combination with those for the thermal hydrolysis of the tetraamine complexes, were interpreted within the combined stoichiometry of Schemes 1 and 3. Rate constants and activation parameters are given in Table 2.

Scheme 3.

Photolyses at 366 nm of the $[Cr(tn)_3]^{3+}$ complex, of cis-$[Cr(tn)_2(tnH)(OH_2)]^{4+}$ and of the cis/trans pentaamine complex mixture were carried out at 25°C. These data, in combination with the data for irradiation of the cis- and trans-tetraamine complexes, were interpreted within the combined stoichoimetry of Schemes 2 and 4. The better defined quantum yields are given in Table 4.

Scheme 4.

The lack of a suitable method for the production of pure pentaamine isomer solutions has so far precluded the extraction of particularly well defined parameters for the thermal and photochemical reactivity of these complexes. The thermal pentaamine formation reactions are reasonably well defined from the stoichiometric experiments referred to above. It appears that only the cis pentaamine is formed directly in significant amounts from the hexaamine complex, and that the cis to trans pentaamine isomerization reaction does not play an important rôle. Inclusion of the thermal interconversion reactions into the stoichiometric reaction scheme gave a singular model from the numerical analysis of the kinetic data. Consequently, these two reactions and the formation of the trans pentaamine isomer from the hexaamine complex were not included in the stoichiometry of Scheme 3.

Table 5. First and second acid dissociation constant for some aqua(1,3-propanediamine)chromium(III) complexes in 1.0 M $NaClO_4$ (standard deviations in parenthesis).

Complex	$-\log [K_a(25°C)/M]$	$\Delta H°/kJ\ mol^{-1}$	$\Delta S°/J\ K^{-1}\ mol^{-1}$
cis-$[Cr(tn)_2(OH_2)_2]^{3+}$	4.778(12)	37(3)	33(10)
	7.442(15)	38(4)	−15(12)
trans-$[Cr(tn)_2(OH_2)_2]^{3+}$	4.096(12)	30(3)	22(10)
	7.668(15)	42(4)	−6(12)
cis-$[Cr(tn)_2(tnH)(OH_2)]^{4+}$	4.66(4)		
	9.70(3) ·		

In Schemes 3 and 4 are included reactions from cis- and trans-$[Cr(tn)_2(tnH)(OH_2)]^{4+}$ to $[Cr(tn)(tnH)_2(OH_2)_2]^{5+}$. These reactions are supposed to be followed by a series of more rapid aquation reactions of the monodentate protonated 1,3-propanediamine ligands to give the $[Cr(tn)(OH_2)_4]^{3+}$ complex as identified by the stoichoimetric ion-exchange experiments.

Reactivity comparisons of the thermal reactions. The general reactivity pattern for amine ligand aquation reactions in chromium(III) complexes established on the basis of data for the complete series of ammine-aquachromium(III) complexes,[2,5] is also seen for the present 1,3-propanediamine complexes. This pattern includes a small but well defined kinetic *trans* effect of an amine ligand as compared to a water ligand, and a tendency towards dominating reactivity contributions from stereoretentive thermal reactions.

The previously noted greater robustness of a chelate 1,3-propanediamine ligand as compared to an ammonia ligand coordinated in the cis-diaminetetraaqua complexes,[4] is seen to be valid also for the isomeric tetraamine complexes and the hexaamine complex. The activation parameters are identical within the estimated standard deviations, and in Table 6 is shown a comparison of aquation rate constants. The behaviour of the chelate diamine ligand is seen to be somewhat different from that of the monodentate protonated 1,3-propanediamine ligand, which is aquated at comparable or faster rates than an ammonia ligand in an analogous complex.

Kinetic parameters for the exchange of coordinated water ligands are similar in the ammonia and the analogous 1,3-propanediamine complexes. This is demonstrated in Table 2 for the stereoretentive exchange reactions of the isomeric tetraamine complexes. Results for the *trans* to *cis* tetraamine isomerization reaction, likely to be the result of a water ligand exchange reaction accompanied by a configurational change, are less well defined and do not allow meaningful comparisons.

The thermal hydrolysis of the $[Cr(tn)_3]^{3+}$ complex and of the isomeric pentaamine complexes have pre-viously been reported in two independent studies at 60°C[6] and at 50°C.[7] The present results are in reasonable agreement with the earlier data for the $[Cr(tn)_3]^{3+}$ and cis-$[Cr(tn)_2(tnH)(OH_2)]^{4+}$ complexes. The agreement between the data for the trans-$[Cr(tn)_2(tnH)(OH_2)]^{4+}$ complex is less satisfactory. This disagreement, however, is as expected, since the previous data were interpreted by less sophisticated stoichiometric reaction schemes.

Reactivity comparisons of the photochemical reactions. Photolysis of solutions of the hexaamine- and the isomeric tetraaminediaquachromium(III) complexes never yields solutions in which significant quantities of complexes with a monodentate protonated amine ligand are present. This might be the reason for a previous report of $[Cr(tn)_3]^{3+}$ yielding cis-$[Cr(tn)_2(OH_2)_2]^{3+}$ directly.[8] This previous study was performed in dilute acidic solution, and the stoichiometry was established from hydrogen ion neutralization data in combination with data for the formation of the free diprotonated diamine. It was attempted to include this path in the present calculations, but the quantum yield was not well defined. All tetraaminediaquachromium(III) formed by photolysis of the hexaamine complex could actually be accounted for by formation through the pentaamine complexes as also noted in Ref. 6. The data for formation of the uncomplexed diamine in Ref. 8 are also well described by secondary photolysis as demonstrated in Fig. 4.

Lack of sufficient quantities of the pure pentaamine-aquachromium(III) isomers has prevented an accurate description of the formation, the aquation and the interconversion reactions of these complexes. From the stoichiometric photolysis experiments it appears, however, that more of the *trans*-pentaamine- than of the cis-pentaamine isomer is formed on irradiation of the hexaamine complex. This is in agreement with a previous report in which identical molar absorption coefficients were assumed by an HPLC-detection technique.[6] The quantum yields for reactions involving the isomeric $[Cr(tn)_2(tnH)(OH_2)]^{4+}$ complexes are given in Table 7. The data are highly correlated, and only few of the

Table 6. Comparison of statistically corrected amine ligand aquation rate constants at 70°C in 1 M $(H,Na)ClO_4$.[a]

Reactant	$10^6 k(NH_3)/s^{-1}$	$10^6 k(tn)/s^{-1}$	$10^6 k(tnH)/s^{-1}$
Cr^III(am)_6	7.9(3)	1.26(2)	—
cis-Cr^III(am)_4(am')(aq)	11.8(2)	3.2(3)	85(10)
trans-Cr^III(am)_4(am')(aq)	11.8(2)	1.3(4)	—
trans-Cr^III(am)_4(am')(aq)	0.0(5)	—	29(8)
cis-Cr^III(am)_4(aq)_2[b]	12.1(3)	2.7(5)	—
cis-Cr^III(am)_4(aq)_2[b]	1.7(3)	0.0(3)	—
trans-Cr^III(am)_4(aq)_2	11.1(2)	1.40(5)	—
fac-Cr^III(am)_2(am')(aq)_3	2.53(10)	—	9(3)
cis-Cr^III(am)_2(aq)_4	1.69(4)	0.325(4)	—
Cr^III(am')(aq)_5	1.108(11)	—	0.66(2)

[a] Data for the ammonia complexes are from Ref. 2. am = am' = NH_3 for the ammonia complexes. $(am)_2$ = tn and am' = tnH⁺ for the 1,3-propanediamine complexes. [b] Formation of fac- and mer-Cr^III(am)_2(am')(aq)_3 respectively.
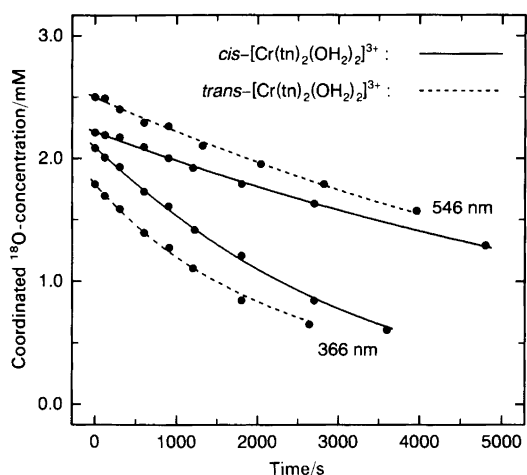
Fig. 3. Photolysis of oxygen-18 labelled cis- and trans-[Cr(tn)$_2$(OH$_2$)$_2$]$^{3+}$ complexes at 366 nm and at 546 nm in 0.5 M HClO$_4$ + 0.5 M NaClO$_4$. The experimental points are obtained from the mass-spectrometric measurements, and the curves are calculated from the concentrations, light intensities and molar absorption coefficients combined with the thermal rate constants and quantum yields from Tables 2–4 and 7.
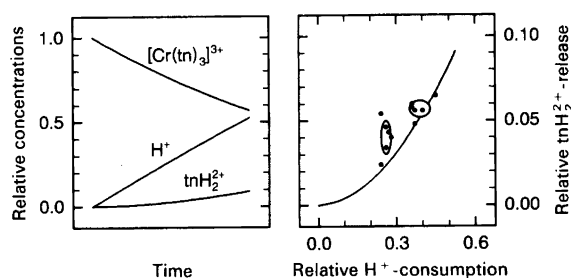

Fig. 4. Left: Calculated hydrogen ion consumption and diamine release during [Cr(tn)$_3$]$^{3+}$ photolysis at 366 nm. The curves are calculated from the quantum yields in Tables 4 and 7. Right: Diamine release vs. hydrogen ion consumption. The curve is obtained from the left part of the figure. Experimental points from Table IV in Ref. 8 are indicated by filled circles, and average values are indicated by contour ellipses of the probability density function drawn at the 68% probability level.

quantum yields are sufficiently well defined to be of value for a detailed discussion. Again experiments starting from the pure trans-pentaamine isomer are definitely needed.

The photoaquation reaction of trans-[Cr(tn)$_2$(tnH)-(OH$_2$)]$^{4+}$ leading to trans-[Cr(tn)$_2$(OH$_2$)$_2$]$^{3+}$ has not been included in the stoichiometric reaction scheme in the final calculations. For analogous, but simpler, systems there is no evidence for this type of stereoretentive aquation reactions, and inclusion did not improve the reproduction of the experimental data. Instead, all the parameters became even more correlated than apparent in Table 7, and had even greater standard deviations, as expected for a nearly singular model.

Photoinduced water exchange in trans-[Cr(tn)$_2$(OH$_2$)$_2$]$^{3+}$ occurs with about the same quantum yield as the photoisomerization reaction. This latter process is most likely the result of a non-stereoretentive water ligand substitution reaction. Consequently, no evidence for stereoretentive water ligand exchange in trans-[Cr(tn)$_2$(OH$_2$)$_2$]$^{3+}$ is available. This further supports previous suggestions that photosubstitution in chromium(III) complexes occurs as the result of a trans-attack of the entering ligand.[9]

Photolyzed solutions of 1,3-propanediamine complexes of chromium(III) contain only minor amounts of species with the monodentate protonated diamine. This is readily apparent both from the stoichiometric experiments and from the data in Tables 4 and 7. This general observation is clearly indicative of the monoprotonated amine being a much better leaving ligand than an amino group of the coordinated chelate diamine ligand. Spectral properties and relevant ligand field parameters are quite similar for ammonia, chelate 1,3-propanediamine and the 3-aminopropyl-1-ammonium ion when coordinated to a chromium(III) centre. This points towards other effects besides those of the ligand field to be of importance for the photochemical reactivity of this class of complexes. This conclusion was also reached on the basis of studies of both the [Cr(en)$_x$(NH$_3$)$_{6-2x}$]$^{3+}$ and the [Cr(tn)$_x$(NH$_3$)$_{6-2x}$]$^{3+}$ series of complexes,[6,10] which established the leaving ligand ability: tn < NH$_3$ < en.

Table 7. Amine ligand photosubstitution and photoisomerization quantum yields for reactions involving the isomeric [Cr(tn)$_2$(tnH)(OH$_2$)]$^{4+}$ complexes in 0.5 M HClO$_4$ + 0.5 M NaClO$_4$ at 25°C irradiated at 366 nm (standard deviations in parenthesis).

Reactant	Product	ϕ/mol einstein^{-1}
[Cr(tn)$_3$]$^{3+}$	cis-[Cr(tn)$_2$(tnH)(OH$_2$)]$^{4+}$	0.04(4)
	trans-[Cr(tn)$_2$(tnH)$_2$(OH$_2$)]$^{4+}$	0.17(4)
cis-[Cr(tn)$_2$(tnH)(OH$_2$)]$^{4+}$	trans-[Cr(tn)$_2$(tnH)(OH$_2$)]$^{4+}$	0.00(6)
	cis-[Cr(tn)$_2$(OH$_2$)$_2$]$^{3+}$	0.18(5)[a]
	trans-[Cr(tn)$_2$(OH$_2$)$_2$]$^{3+}$	0.094(13)[a]
	?-[Cr(tn)(tnH)(OH$_2$)$_3$]$^{4+}$	0.010(5)
trans-[Cr(tn)$_2$(tnH)(OH$_2$)]$^{4+}$	cis-[Cr(tn)$_2$(tnH)(OH$_2$)]$^{4+}$	0.13(11)
	cis-[Cr(tn)$_2$(OH$_2$)$_2$]$^{3+}$	0.12(6)

[a] Quantum yields for the competitive formation of the isomeric tetraaminediaqua isomers have earlier been reported with somewhat smaller standard deviations.[12] These earlier calculations were performed without the pentaamine isomerization reactions, and the present values, although less well defined, should be preferred.

Triamine species are even less dominant reaction products in the photolysis of the isomeric tetraaminediaquachromium(III) isomers than pentaamine products are in the hexaamine photolysis experiments. Triamine complexes have not been observed in sufficient quantities during the photolysis experiments for an accurate characterization. The photochemical reactions of *cis*- and *trans*-$[Cr(tn)_2(OH_2)_2]^{3+}$ appear to give $[Cr(tn)(OH_2)_4]^{3+}$ directly, but this occurs most likely *via* the isomeric *fac*- and/or *mer*-$[Cr(tn)(tnH)(OH_2)_3]^{4+}$ complexes. Since the triamine complex products could not be characterized, the relative reactivity contributions could not be determined. This also applies to the minor amounts of triamine species formed via the $5+$ charged tetraaminediaquachromium(III) mixture of isomers.

Mechanism of excited state deactivation. Different product distributions for thermal and for photochemical reactions is a characteristic feature in the chemistry of chromium(III) complexes. This phenomenon has been labelled an 'antithermal' behaviour of the photochemical reactions, and is also observed in the present reactions. Accurate characterization of competing thermal and photochemical reactions in the ammineaquachromium(III) series of complexes has questioned this 'antithermal' labelling with reference to the correlation between a higher enthalpy of activation and a more dominating photochemical, ϕ, than thermal, k, reactivity contribution, i.e. $\phi_a/\phi_b > k_a/k_b$ for $\Delta H_a^* > \Delta H_b^*$ for two competing processes labelled a and b.[1] This behaviour is also seen for the present chromium(III) complexes, although the complexity of the system has prevented most of the parameters from being sufficiently accurate to be informative.

The photochemical reactivity of $[Cr(tn)_3]^{3+}$ has earlier been investigated in basic solution.[8,11] Under these conditions the major reactivity contribution, corresponding to that of the excited doublet state, is quenched by OH^-, but the excited quartet state remains reactive. This latter state has been found to give a significantly higher *cis/trans* pentaamineaquachromium(III) isomer ratio than the excited doublet state, and this ratio has also been reported to be wavelength-dependent. It was concluded that the photochemical reaction arising from the excited quartet state occurred in competition with vibrational relaxation,[11] but no explanation has been offered with regard to the formation of the *cis* isomer being favoured by the quartet state reaction.

It has earlier been pointed out that the ligand field gives a significant *negative* contribution to the enthalpy of activation for reactions of components of the lowest, $^4T_2(O_h) \leftarrow {}^4A_2(O_h)$, excited state. The magnitude of this contribution depends partly upon the Δ-values of the ligands involved in the reacting plane, and partly on the angular distortions in this plane. This latter contribution is numerically larger for ligand sets which allow the formation of a symmetry axis of uneven symmetry.[13]

The limiting cases can be represented by trigonal or pentagonal bipyramids for the limiting dissociative or associative intimate mechanisms. The ligand field contributions for these two cases are most similar and cannot be used to discriminate between the two mechanisms. An important consequence of such considerations, and the fact that chelate ligands coordinated with bite angles around 90° seldom allow distortions to give 120 or 72° bite angles, is that the presence of a chelate ligand in the reacting plane will give a *positive* contribution to the enthalpy of activation. This could not be expected to be very important for the excited quartet state reactivity, for which the net result will still be negative. For the doublet state, however, it has been proposed that the solvent-assisted reactive deactivation occurs by back intersystem crossing to the reactive quartet state. The probability for an efficient intersystem crossing depends upon a small quartet-to-doublet state energy separation, which in turn is a function of geometrical distortions leading to a quartet state energy lowering. This may be expected to take place more easily for a reaction which leads to the *trans* pentaamine isomer in which bond stretching to an in-plane chelate leaving ligand may relieve the strain of an otherwise unfavourable chelate ligand situation, than for a reaction that leads to the *cis* isomer in which the bond stretching will occur to an out-of-plane chelate ligand, in agreement with the experimental result.

It is important to realize that the above ligand field rationalization is concerned only with the *relative* doublet vs. quartet product formation and does not give an explanation for the overall preference for *cis* isomer formation from the excited quartet state. This latter problem is intimately connected with predictions of leaving ligand abilities, which is still much debated. The reactivity comparison from the present data involving water and chelate 1,3-propanediamine points towards important energy contributions for the metal–ligand bond breaking reactions that may be similar for the reactions in the electronic ground state and in the excited state. This conclusion, previously arrived at by comparative studies of the ammineaquachromium(III) series of complexes,[1] also appears to be valid for the comparative studies of complexes of 1,2-ethanediamine, ammonia and 1,3-propanediamine.[4,6,10]

Experimental

Caution! The perchlorate salts described here are potentially explosive and should be handled accordingly.

Chemicals. $[Cr(tn)_3]Br_3$, *cis*-$[Cr(tn)_2Cl_2]ClO_4$, *trans*-$[Cr(tn)_2Cl_2]Cl$ and $Ag(tos)$ were prepared by modified literature methods.[5,14] $NaClO_4$, for the medium for the potentiometric titrations, was recrystallized from water. The sources of other chemicals have been described earlier.[1]

Preparation of solutions for the thermal and photochemical experiments.

[Cr(tn)₃]³⁺. The hexaamine solutions were prepared by dissolving the tris(1,3-propanediamine)chromium(III) compound in the reaction medium.

cis- and *trans-[Cr(tn)₂(OH₂)₂]³⁺.* The tetraamine solutions were prepared by dissolving about 300 mg of the dichlorobis(1,3-propanediamine)chromium(III) compound in 10 ml of water at room temperature. 1 ml 2M mercury(II) perchlorate in 0.5 M perchloric acid was added to the aqueous complex solution, and this mixture was allowed to react until an orange solution had been formed. This occurred rapidly for the *cis* isomer but was a somewhat slower process in the case of the *trans* compound, which initially precipitates the perchlorate salt. The excess of mercury(II) was then reacted with 2 ml 1 M NaBr. The resulting mixture was filtered into 100 ml of water and the filtrate charged onto a Sephadex SP-C-25 ion-exchange column. Purification by elution with a mixture of 1.0 M NaClO₄ and 0.01 M HClO₄ was performed as described earlier for the ammine-aquachromium(III) complexes.[15]

Solutions for the potentiometric titrations were neutralized to a hydrogen ion concentration of about 0.001 M with aqueous sodium hydroxide prior to the filtration, and were eluted without added perchloric acid in the elution solvent.

cis-[Cr(tn)₂(tnH)(OH₂)]⁴⁺. About 500 mg [Cr(tn)₃]Br₃ were dissolved in 10 ml 0.1 M HClO₄ and kept in the dark at 60°C for 18 h. The resulting solution was cooled to room temperature, diluted with water to about 150 ml and charged onto a Sephadex SP-C-25 ion-exchange column. Unreacted hexaamine complex and other 3+ charged ions were removed by elution with 0.5 M NaClO₄ + 0.01 M HClO₄. After elution of the 3+ charged components the remaining 4+ charged species were eluted with 1.0 M NaClO₄ + 0.01 M HClO₄.

The *cis*-pentaamine solutions for the potentiometric titrations were made by neutralizing the reaction solution to a hydrogen ion concentration of about 0.001 M with sodium hydroxide solution prior to the dilution with water. The following separations were performed with NaClO₄ solutions without added perchloric acid.

FPLC analyses of such solutions showed less than about 3% of the *trans* isomer.

cis/trans-[Cr(tn)₂(tnH)(OH₂)]⁴⁺ mixture. About 500 mg [Cr(tn)₃]Br₃ were dissolved in 10 ml 0.1 HClO₄ and irradiated in bright sunlight for some hours until conversion of about 20% of the hexaamine had occurred. The resulting mixture was separated as described above for the pure *cis*-pentaamine isomer.

In some experiments controlled photolysis at 366 nm of about 100 mg [Cr(tn)₃]³⁺ in 10 ml 0.1 M perchloric acid

was carried out at 25°C to a hexaamine conversion degree of about 25%. Solutions prepared by the different methods had similar spectral characteristics.

fac/mer-[Cr(tn)(tnH)(OH₂)₃]⁴⁺ mixture. A solution of *cis*-[Cr(tn)₂(OH₂)₂]³⁺ prepared as described above was made 0.1 M in perchloric acid and was kept at 75°C for 24 h in the dark. Isolation of the 4+ charged components was performed as described above for the *cis*-[Cr(tn)₂(tnH)(OH₂)]⁴⁺ complex. Fractionation of the eluate of 4+ charged species showed that the *mer* isomer is eluted prior to the *fac* triamine isomer.

[Cr(tn)(OH₂)₄]³⁺, [Cr(tnH)(OH₂)₅]⁴⁺ and [Cr(OH₂)₆]³⁺ were prepared in solution as described previously.[4]

Preparation of ¹⁸OH₂-enriched complexes. About 100 mg of the *cis-* or *trans-*[Cr(tn)₂Cl₂]⁺ complex salt were treated with about 300 mg silver tosylate in 1 ml ¹⁸OH₂ with an isotopic purity of about 95% for about 15 min at 50°C and then for about 45 min at room temperature. The excess of ¹⁸OH₂ was recovered by vacuum sublimation, the excess of silver(I) was precipitated as insoluble silver(I) bromide, and the [Cr(tn)₂(OH₂)₂]³⁺ complex solutions were purified in the dark as described above. The prepared complexes had an isotopic purity of about 70%.

Thermal experiments. Aliquots of solutions were sealed in a suitable number of glass ampoules and were immersed into a thermostatted water bath maintained at the desired temperature with an accuracy of ±0.05°C. During the progressing hydrolysis the solutions were protected from light. At suitable time intervals ampoules were withdrawn from the thermostat, and the reactions quenched by cooling the reaction mixtures in an ice bath. The spectra were measured at 700–300 nm.

Solutions for the water exchange experiments were protected from light and placed in a thermostatted water bath. 10 ml samples were withdrawn at suitable time intervals and rapidly frozen. The ¹⁸O-content of the solvent water was determined mass-spectrometrically as described previously.[5]

Photochemical experiments. The photochemical experiments were performed by a continuous photolysis technique using cylindrical quartz cells thermostatted at 25°C and light at 366 nm selected from a high-pressure mercury lamp by means of a Spindler and Hoyer interference filter.[16] Light intensities were determined by ferrioxalate actinometry.[17] Quantum yields were determined by photolysis of 12.8 ml portions of about 2 mM solutions of the 3+ charged species or about 1 mM solutions of the 4+ charged species. The photoreactions were interrupted periodically for spectrophotometric measurements.

Water exchange quantum yields were determined by photolysis of 12.8 ml of a solution of the ¹⁸O-enriched

complex at 366 and 546 nm. 10.0 ml aliquots of the photolyzed solution were quickly frozen in liquid nitrogen and subsequently prepared for mass spectrometric analysis by sublimation in vacuum.[5] Light intensities were determined by ferrioxalate actinometry at 366 nm,[17] $\phi \approx 1.21$ mol einstein^{-1}, and by Reinecke salt actinometry at 546 nm,[18] $\phi \approx 0.282$ mol einstein^{-1}.

Determination of acid dissociation constants. This was performed by titrations at 25 and 40°C.[19] The results are given in Table 5.

Method of calculation. The calculations were all made within the framework of non-linear regression analysis. This has earlier been described in detail for both photochemical[1,16] and thermal experiments.[20]

Visible absorption spectra were recorded on a Cary Varian 219 spectrophotometer or on an RC-Partner computer-controlled Perkin-Elmer Lambda-17 spectrophotometer.

Methods of analysis and mass spectrometric measurements. These have been described.[5,15]

FPLC-analyses were performed using a Pharmacia FPLC apparatus equipped with a Mono S HR 5/5 column. Gradient elution from aqueous 0.01 M HBr to aqueous 0.01 M HBr + 0.99 M NaBr were used for the separations.

References

1. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 40* (1986) 637.
2. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 28* (1974) 569.
3. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 29* (1975) 29.
4. Mønsted, L. *Acta Chem. Scand., Ser. A 30* (1976) 599.
5. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 34* (1980) 259.
6. Kirk, A. D. and Ibrahim, A. M. *Inorg. Chem. 27* (1988) 4567.
7. Cimolino, M. C. *Ph.D. Thesis*, University of California, San Diego, CA 1982.
8. Gowin, E. and Wasgestian, F. *Inorg. Chem. 24* (1985) 3106.
9. Kirk, A. D. *Mol. Photochem. 5* (1973) 127.
10. Kirk, A. D., Frederick, L. A. and Wong C. F. C. *Inorg. Chem. 18* (1979) 448.
11. Kirk, A. D. and Ibrahim, A. M. *Inorg. Chem. 29* (1990) 4848.
12. Mønsted, L. and Mønsted, O. *Pure Appl. Chem. 62* (1990) 1095.
13. Mønsted, L. and Mønsted, O. *Coord. Chem. Rev. 94* (1989) 109.
14. Pedersen, E. *Acta Chem. Scand. 24* (1970) 3362.
15. Mønsted, L. and Mønsted, O. *Acta Chem. Scand. 27* (1973) 2121.
16. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 38* (1984) 679.
17. Hatchard, C. G. and Parker, C. A. *Proc. R. Soc. London, Ser. A 235* (1956) 518.
18. Wegner, E. E. and Adamson, A. W. *J. Am. Chem. Soc. 88* (1966) 394.
19. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 30* (1976) 203.
20. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 32* (1978) 19.