

Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. VI. Acid Dissociation and Structure of 1,4,7,10-Tetraazadecanechromium(III) Complexes in Aqueous Perchloric Acid

L. MØNSTED and O. MØNSTED

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

The chromium(III) 1,4,7,10-tetraazadecane ($H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$) species postulated by earlier workers to be the *mer*-triqua(1-azonia-4,7,10-triazadecane) chromium(III) ion has been shown by potentiometric titrations to be the *cis*-diaqua(1,4,7,10-tetraazadecane)chromium(III) ion. Acidity constants and visible absorption spectra of this tetraamine ion are reported and compared with values for other tetraaminediaquachromium(III) species. Reinterpretation of earlier kinetic data necessitated by the above reformulation reveals not only that dechelation in acid solution of the 1,4,7,10-tetraazadecane ligand bound to chromium(III) takes place preferentially from the secondary amino groups, but also that the species thus initially formed reacts rapidly further to give a diaminetetraaquachromium(III) species.

For chromium(III) hydrolysis and isomerization reactions quantitative kinetic data exist in the literature for complexes of amine ligand pairs of the type $RR'NH$ and $RR'NCH_2CH_2NH_2^+$. A summary of these data is given in Table 1. The pronounced difference between the kinetic behaviour of the first three reactant pairs and that attributed to the *mer* complexes is noteworthy. To us, this difference appeared difficult to explain in terms of the accepted structures of the reactants, and therefore it was decided to investigate the chromium(III) 1,4,7,10-tetraazadecane complexes in greater detail.

EXPERIMENTAL

Chemicals. Most chemicals employed have been described earlier.^{5,6} *cis*-[Cr(trien)Cl₂]Cl⁷ and *cis*-[Cr(trien)F₂]ClO₄⁸ were prepared according to literature methods and the latter compound converted to *cis*-[Cr(trien)Cl₂]ClO₄ and *cis*-[Cr(trien)Br₂]ClO₄ by reacting the difluorido compound with concentrated hydrochloric or hydrobromic acid, respectively.⁹

Preparation of solutions. Preparation of the tetraamine- and the bis(1,2-ethanediamine)-chromium(III) solutions employed in the titration experiments have been described earlier.^{5,6} *cis*-Diaqua(1,4,7,10-tetraazadecane)chromium(III). About 100 mg of solid *cis*-dibromido(1,4,7,10-tetraazadecane)chromium(III) perchlorate was treated with 1 ml 1 M sodium hydroxide solution for 3 min at room temperature. The resulting solution was cooled in ice and acidified with 70 % perchloric acid. Unreacted dibromidoperchlorate complex was filtered off, and after dilution to about 10 ml with water the solution containing the complex was charged onto a 2 cm × 10 cm SP-Sephadex C-25 column. The column was operated at 0 °C and 0.75 M sodium perchlorate solution made 1–3 mM acid with perchloric acid eluted the different chromium(III) 1,4,7,10-tetraazadecane complexes essentially as described by Garner *et al.*¹⁰ except that these authors used 1.25 to 4 M perchloric acid and Dowex AG50 W-X2 columns.

fac-Triqua(1-azonia-4,7,10-triazadecane)-chromium(III). A mixture of this ion and the *cis*-diaminetetraaquachromium(III) isomers of the tetraamine ligand was prepared by rapidly heating an acid solution of impure tetraaminediaquachromium(III) ions, prepared by the method described above, to 100 °C and then

Table 1. Rate constants for reactions of some amine aqua chromium(III) complexes.

Complex ^a	10 ⁴ k (60 °C) (s ⁻¹)	Rate constant ratio	Ref.
Hydrolysis reactions			
[Cr(a)(aq) ₅] ³⁺	0.31	0.17	1
[Cr(enH)(aq) ₅] ⁴⁺	1.9		2
[Cr(en)(aq) ₄] ³⁺	3.0	0.14	2
[Cr(dienH)(aq) ₄] ⁴⁺	22		3
<i>fac</i> -[Cr(dien)(aq) ₃] ³⁺	59	0.45	3
<i>fac</i> -[Cr(trienH)(aq) ₃] ⁴⁺	130		4
<i>mer</i> -[Cr(dien)(aq) ₃] ³⁺	16 000	13	3
<i>mer</i> -[Cr(trienH)(aq) ₃] ⁴⁺	1 200		4
Isomerization reactions			
<i>mer</i> -[Cr(dien)(aq) ₃] ³⁺	unobserved		3
<i>mer</i> -[Cr(trienH)(aq) ₃] ⁴⁺	370		4

^a The following abbreviations for the names of the ligands are used throughout this paper: a = ammonia, aq = water, en = 1,2-ethanediamine, enH = 2-aminoethylammonium ion, dien = 1,4,7-triazaheptane, dienH = 1-azonia-4,7-diazaheptane, trien = 1,4,7,10-tetraazadecane, and trienH = 1-azonia-4,7,10-triazadecane.

rapidly cooling the solution. From this mixture the individual complexes were prepared pure in solution by the chromatographic method described above for the tetraaminediaqua complex.

The visible absorption spectra of the solutions prepared by the above methods are given in Fig. 1. From the spectral characteristics in Table 2 it is concluded that the species generated by base hydrolysis of the *cis*-dibromido-(1,4,7,10-tetraazadecane)chromium(III) ion is identical to the one produced either by base hydrolysis or by mercury(II) accelerated chloride ligand hydrolysis of the *cis*-dichlorido-(1,4,7,10-tetraazadecane)chromium(III) ion.¹⁰

Spectral measurements. All visible absorption spectra were measured on a modified Cary 118C spectrophotometer at room temperature (23 ± 2 °C).

Potentiometric measurements. The pH measurements were carried out using a Radiometer PHM52 pH-meter equipped with a G202C glass electrode and a K401 calomel electrode both also from Radiometer. In the latter electrode the initial saturated potassium chloride electrode solution was replaced with 1.0 M sodium chloride solution. All measurements were carried out at 25.00 ± 0.05 °C, by titrating 25 ml of solutions 1 to 4 mM in chromium complex and 1.0 M in sodium perchlorate by 1.0 M sodium hydroxide solution. Since the complexes studied decompose noticeably at 25 °C fast titrations and consequently rapid electrode response were essential. For the electrode used pH measurements less than a 0.001 pH-unit from the final reading was obtained in less than 5 s. Conse-

quently full titration curves of approximately 30 to 40 individual measurements could be obtained in 5–10 min.

Methods of analysis were essentially as described previously.¹

Method of calculation. The primary experimental material for one titration curve con-

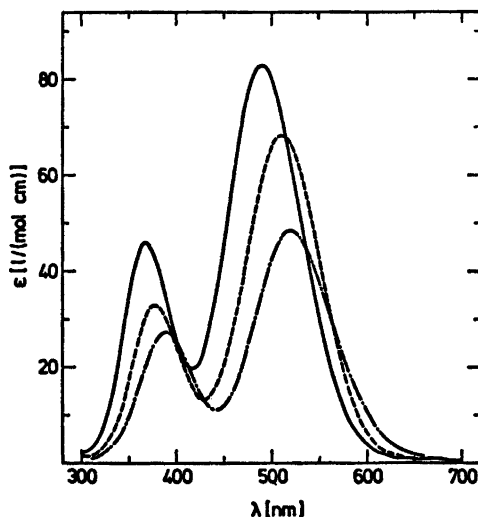


Fig. 1. Visible absorption spectra of compounds prepared and purified as described in the text. —, *cis*-[Cr(trien)(aq)₃]³⁺; - - -, *fac*-[Cr(trienH)(aq)₃]⁴⁺; and - · -, *cis*-[Cr(trienH₃)(aq)₃]⁴⁺.

Table 2. Comparison with literature values of spectral characteristics of compounds prepared and purified as described in the text.

Complex	Medium ^a	λ_1 max (nm)	ϵ_1 max [l/(mol cm)]	λ_2 max (nm)	ϵ_2 max [l/(mol cm)]	ϵ_1 max/ ϵ_2 max	Ref.
<i>cis</i> -[Cr(trien)(aq)] ³⁺	A	490	82.7	367	45.4	1.82	^b
	B	493	82.9	368	45.5	1.82	10 ^c
<i>fac</i> -[Cr(trienH)(aq)] ⁴⁺	A	511	67.8	375	32.9	2.06	^b
	B	513	72.0	375	35.6	2.02	10
<i>cis</i> -[Cr(trienH ₂)(aq)] ⁵⁺	A	520	48.2	388	27.1	1.78	^b
	B	522	48.7	389	27.5	1.77	10

^a A, 0.5 M HClO₄ + 0.4 M NaClO₄; B, 2 M HClO₄. ^b This work. ^c Reported as *mer*-[Cr(trienH)(aq)]⁴⁺ in this reference.

sisted of one initial volume, one base titrator concentration, and a series of potential differences (E) measured as function of the volume of added base (v), as well as estimated variances upon these same quantities (σ_E^2, σ_v^2).

Parameters were estimated by regression analysis, which for practical purposes for these data is equivalent to minimization of:

$$s^2 = \sum \{ [E(\text{obs}) - E(\text{calc})]^2 / (\sigma_E^2 + \left(\frac{dE}{dv}\right)^2 \sigma_v^2) \}$$

where the summation extends over all experiments of one titration curve.

The potential differences were calculated from the hydrogen ion concentrations of the solutions, and the hydrogen ion concentrations were calculated from the acidity constants of the weak acid investigated, the ionic product of water and the concentrations of weak acid and excess strong acid in the initial solution. Combination of the relevant mass action expressions with the expression for the potential differences in terms of the hydrogen ion concentrations in the initial solution (h_0) and in the i 'th solution (h_i):

$$E_i = \Delta E + \alpha RT \ln \{ (h_i + \gamma) / (h_0 + \gamma) \} / F \quad (1)$$

yielded a nonlinear equation which was solved by Newton's algorithm. In eqn. 1 α and γ are measures of glass electrode deviations from ideal behaviour in terms of a reduced response ($\alpha RT/F$) relative to that expected theoretically (RT/F), and sodium ion error (γ), taken to be constant since only solutions with the sodium ion concentration equal to 1.0 mol/l were investigated. The term governed by the ΔE parameter is necessary as a fitting term since standardized potentials were not measured, as we were only interested in concentration acidity constants. For a divalent acid eight parameters were consequently to be determined. This was accomplished without difficulty from

initial parameter values estimated by inspection of the titration curves. In Fig. 2 is shown the agreement between the experimental and the calculated titration curves for the *cis*-diaqua(1,4,7,10-tetraazadecane)chromium(III) complex.

It was not attempted to estimate the absolute magnitudes of σ_E and σ_v . The variances were, however, assumed to be constant for all titration points. Then only the ratio $\sigma_E \sigma_v$ was essential to the calculations and it was estimated to have the value 1.5 mV/ μ l (cf. Fig. 2). Since

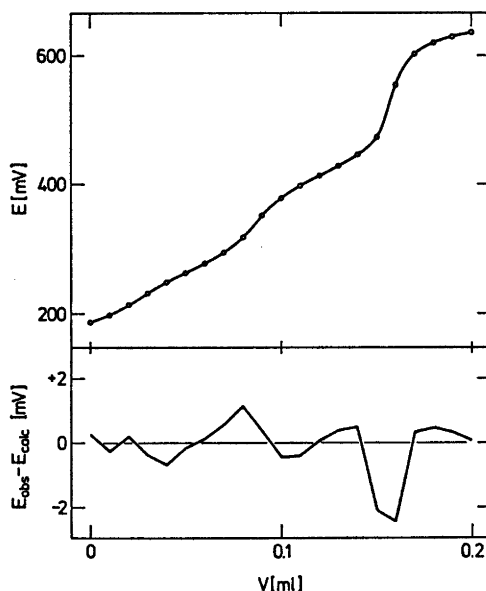


Fig. 2. Upper part: Experimental (O) and calculated (—) titration curve for *cis*-[Cr(trien)(aq)]³⁺. Lower part: Differences between experimental and calculated titration curves.

absolute values for the variances were not estimated, a χ^2 test of the goodness of the fit between experiments and model could not be carried out. A reverse estimation is however possible, and it was found that in order to have $P\{\chi^2 < s^2\} \sim 50\%$, a value of σ_E about 0.4 mV is estimated. This value is not unreasonable, in particular if the somewhat unstable systems are borne in mind.

The calculational approach outlined above parameterizes a fair amount of possible systematic errors as, e.g., strongly acid or basic impurities in the medium or the solid salts employed. Also the utilization of concentration acidity constants as well as the direct determination of the α parameter from the titration curves eliminates all systematic errors associated with the use of standard buffer solutions. It was also attempted to parameterize possible systematic errors due to absorbed carbon dioxide in solvent and sodium hydroxide titrator solution. For this the acid dissociation constants of carbon dioxide measured by Sillén *et al.*¹¹ ($pK_1 \sim 6.04$ and $pK_2 \sim 9.57$) in 1 M sodium perchlorate solution at 25 °C were used. The agreement between model and experiments was, however, not significantly improved, and from the estimated parameter values it seemed as if the parameter values rather than arising from carbon dioxide should be attributed to minor amounts of ammonia or amines generated by decomposition reactions of the investigated complexes. It was, however, reassuring to note the independence of the estimated acid dissociation constants upon this kind of systematic error.

These estimated concentration acid dissociation constants, determined from at least two full titration curves for each complex, are given in Table 3. In addition to these parameters the following ones, common to all the experiments were estimated: $\alpha \sim 0.964 \pm 0.008$, $\gamma \sim 10^{-13.08 \pm 0.09}$ mol/l and $K_w \sim 10^{-13.82 \pm 0.07}$ mol²/l². Of these parameters the first two appear reasonable and the last is essentially in agreement with the values $10^{-13.80}$ mol²/l²¹² and $10^{-13.95}$ mol²/l²,¹³ earlier determined in a 1.0 M sodium perchlorate

medium. By inspection of these parameters and those of Table 3 the estimated standard deviations of both the $\log K_w$ and $\log K_1$ values are seen to be somewhat larger than those estimated for the $\log K_1$ values, as is to be expected.

RESULTS AND DISCUSSION

The titration curve, given in Fig. 2, of the species generated by base hydrolysis of the *cis*-dibromido(1,4,7,10-tetraazadecane)chromium(III) ion shows that it is a divalent acid. The close similarity between the acid dissociation constants of this ion and the *cis*-tetraaminediaqua- and the *cis*-diaquabis(1,2-ethanediamine)chromium(III) ions given in Table 3 confirms our hypothesis that the species in question is not a *mer* triaqua complex as claimed earlier, but rather the *cis*-diaqua(1,4,7,10-tetraazadecane)chromium(III) ion.

Additional but less conclusive evidence comes from comparisons between elution behaviour and spectral characteristics of 1,4,7,10-tetraazadecane- and 1-azonia-4,7,10-triazadecane complexes which might reasonably be expected to resemble bis(1,2-ethanediamine)- and (2-aminoethylammonium)(1,2-ethanediamine) complexes, respectively.

Since the *mer*- and *fac*-(2-aminoethylammonium)triaqua-(1,2-ethanediamine)chromium(III) complexes are only partly separated by the technique which clearly separates these two ions from the *cis*-diaquabis(1,2-ethanediamine)chromium(III) complex and also separates the *fac*-triaqua(1-azonia-4,7,10-triazadecane)chromium(III) ion from the complex ion in question, a tripositive tetraaminediaqua structure of the latter complex is a reasonable

Table 3. Estimated concentration acidity constants (mean values \pm standard deviations of the mean values) for some *cis*- and *trans*-tetraaminediaquachromium(III) complexes in 1.0 M sodium perchlorate solution at 25 °C.

Complex	$-\log K_1^a$	$-\log K_2^a$
<i>cis</i> -[Cr(a) ₄ (aq) ₂] ³⁺	4.961 \pm 0.015	7.53 \pm 0.03
<i>cis</i> -[Cr(en) ₂ (aq) ₂] ³⁺	4.75 \pm 0.03	7.35 \pm 0.05
<i>cis</i> -[Cr(trien)(aq) ₂] ³⁺	4.47 \pm 0.03	7.14 \pm 0.05
<i>trans</i> -[Cr(a) ₄ (aq) ₂] ³⁺	4.376 \pm 0.014	7.78 \pm 0.04
<i>trans</i> -[Cr(en) ₂ (aq) ₂] ³⁺	4.118 \pm 0.015	7.71 \pm 0.05

^a The K 's are measured in mol/l.

Table 4. Comparison between spectral characteristics of some *cis*-bis(1,2-ethanediamine)- and some *cis*-(1,4,7,10-tetraazadecane)chromium(III) complexes.

Complex	λ_1 max (nm)	λ_2 max (nm)	Ref.
<i>cis</i> -[Cr(en) ₂ F ₂] ⁺	517	378	14
<i>cis</i> -[Cr(trien)F ₂] ⁺	523	374	8
<i>cis</i> -[Cr(en) ₂ Cl ₂] ⁺	528	401	^a
<i>cis</i> -[Cr(trien)Cl ₂] ⁺	534	397	^a
<i>cis</i> -[Cr(en) ₂ (aq) ₂] ³⁺	486	368	6
<i>cis</i> -[Cr(trien)(aq) ₂] ³⁺	490	367	^a

^a This work.

supposition. This view is also supported by the fact that spectral differences similar to those observed for the difluorido and dichlorido tetraamine pairs both of known constitution are also found when the supposed *cis*-diaqua-(1,4,7,10-tetraazadecane) complex is compared to the *cis*-diaquabis(1,2-ethanediamine) complex. In all three cases the first spin allowed absorption band is shifted towards the red and the second towards the blue when the 1,4,7,10-tetraazadecane complexes are compared to the bis(1,2-ethanediamine) complexes (Table 4). Further evidence comes from a comparison between some isomeric triaminetriaquachromium(III) complexes. For the isomer pairs of known constitution a spectral shift towards the red of the second spin-allowed absorption band of *mer* isomers compared to the corresponding *fac* isomers has been observed (Table 5). This fact also makes it less likely that the species investigated is a *mer*-triaminetriaqua isomer.

The reformulation of the structure of the initial reactant species of the earlier kinetic

Table 5. Comparison between the position of the second spin-allowed absorption band of some isomeric triaminetriaqua chromium(III) complexes.

Complex	λ_2 <i>fac</i> (nm)	λ_2 <i>mer</i> (nm)	Ref.
[Cr(a) ₃ (aq) ₃] ³⁺	374	376	5
[Cr(en)(enH)(aq) ₃] ⁴⁺	378	380	6
[Cr(dien)(aq) ₃] ³⁺	375	390	10
[Cr(trienH)(aq) ₃] ⁴⁺	375	[367] ^a	10

^a This value refers to *cis*-[Cr(trien)(aq)₃]³⁺ which in Ref. 10 is supposed to be the *mer*-[Cr(trienH)(aq)₃]⁴⁺ ion.

investigations necessarily leads to a modification of the reaction scheme. The fact that both *fac*-triamine- and *cis*-diaminechromium(III) ions are produced simultaneously from the tetraamine isomer, combined with the generally accepted hypothesis that multiple metal ligand bond breaking reactions occur stepwise, makes it necessary to postulate the existence of a triamine species different from the one actually isolated from hydrolyzed tetraamine solutions. The simplest hypothesis about the structure of this species is, that it is a triamine isomer formed by hydrolysis of a secondary amine nitrogen atom. Intuitively this hypothesis rationalizes the high reactivity because of which this species has so far escaped detection. The reformulated reaction scheme is shown in Fig. 3. It should be noted that this modification of the reaction scheme in no way affects the numerical values for rate constants or activation energies but assigns these values to other reactions. The possibility may now be envisaged that a reinterpretation similar to the one given here

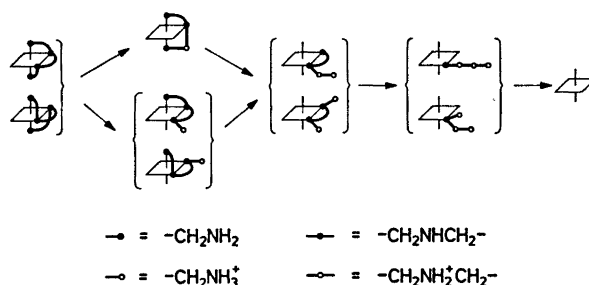


Fig. 3. Reaction scheme so far elucidated for the acid hydrolysis of 1,4,7,10-tetraazadecane complexes of chromium(III) (see text).

for the aqua-1,4,7,10-tetraazadecane complexes may also apply to the kinetic results for the aquaazido-1,4,7,10-tetraazadecane complexes,¹⁵ in which system the initial reaction is said exclusively to be a *mer* to *fac* isomerization reaction.

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