Contribution No. 2045 from the Department of Chemistry, University of California, Los Angeles, California 90024

Transition Metal Complexes of Triethylenetetramine. IV. Synthesis of Chloroaquotriethylenetetraminechromium (III) Cation, and Kinetics of Primary and Secondary Aquation of *cis-α*-Dichlorotriethylenetetraminechromium (III) Cation [1a, 1b]

Cecilia Y. Hsu and Clifford S. Garner

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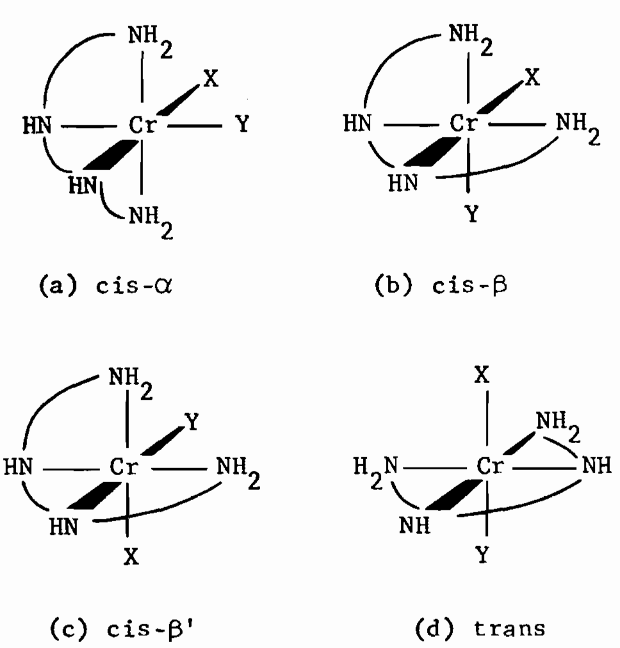
The new complex, pink Cr(trien) $(OH_2)Cl^{2+}$ (probably cis-β *or* cis-β′ *isomer), has been synthesized and characterized in aqueous solution, as have orange Cr(trien) $(OH_2)_2^{3+}$ (unknown isomers) and a purple species tentatively characterized as Cr(trienH) $(OH_2)_2Cl^{3+}$ (unknown isomers), and their visible absorption spectra recorded. The latter two species are directly formed products in the hydrolysis of pink Cr(trien) $(OH_2)Cl^{2+}$ in 0.1-3* F $HClO_4$ *at 25-35°. Aquation of* cis-α-*Cr(trien)Cl_2^+ follows a first-order rate law with* k = *(1.92 ± 0.06) × 10^{-4} sec^{-1} at 25.00° over the range 0.001-0.1* F $HClO_4$ *(μ = 0.1);* E_a= *21.2 ± 0.7 kcal $mole^{-1}$ and log* PZ = *11.8 ± 0.5 (sec^{-1}). The aquation product is the new pink chloroaquo complex. Reaction schemes and approximate rate constants are presented for the hydrolysis of the chloroaquo complex. Comparisons of rates are made with Cr(III)-bis(en) and Co(III)-trien analogs where they are known.*

Introduction

In the past ten years increasing numbers of chromium(III) amine complexes have been prepared, some of them with interesting multidentate amine ligands. As part of a program to compare the products, stereochemistry and rates of aquation of such complexes with one another and with their cobalt(III) analogs, an investigation was undertaken of the primary and secondary aquation of the recently synthesized *cis*-α-dichlorotriethylenetetraminechromium(III) cation, *cis*-α-Cr(trien)Cl_2^+ [2,3], in aqueous perchloric acid. Disubstituted triethylenetetraminechromium(III) complexes with two different monodentate ligands X and Y can each exist theoretically in four geometric isomeric forms, as shown in Figure 1. Thus, *cis*-α-Cr(trien)Cl_2^+ (Figure 1a, with X = Y = Cl) is identical with the well-known *cis*-Cr(en)$_2$$Cl_2^+$ except for a bridging CH_2CH_2 group, and the kinetic and stereochemical consequences of this additional chelation in the triethylenetetramine complex are of interest. This study also provides another opportunity to see if side reactions involving Cr-N bond breakage compete significantly with Cr-X (X = halogen or pseudohalogen) bond breakage, as has been observed in some related chromium(III) amine complexes [4-9], but apparently not in the cobalt(III) analogs.



(a) cis-α (b) cis-β (c) cis-β′ (d) trans

Figure 1. Theoretically possible geometric isomers of Cr(trien)XY^{n+} complexes.

In the present paper we report the results of this study, together with the synthesis of a new complex, the chloroaquotriethylenetetraminechromium(III) cation (probably *cis*-β or *cis*-β′), and evidence for a derivative species in which one Cr-N bond has broken and for a diaquotriethylenetetraminechromium(III) species. Related visible absorption spectra are also presented.

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(1) (a) Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University. This paper constitutes Report No. UCLA-34P12-58 to the A.E.C. (b) Based partly upon the M.S. Thesis (UCLA, 1966) of Cecilia Y. Hsu.

(2) D. A. House and C. S. Garner, *J. Am. Chem. Soc.*, *88*, 2156 (1966); Part III of this series.

(3) Abbreviations used: en = ethylenediamine, $H_2N(CH_2)_2NH_2$; trien = triethylenetetramine, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$.

(4) C. S. Garner and D. J. MacDonald, in S. Kirschner (Ed), «Advances in the Chemistry of the Coordination Compounds», Macmillan Co., New York, 1961, pp. 266-275.

(5) D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, *83*, 4152 (1961).

(6) D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, *1*, 20 (1962).

(7) D. C. Olson and C. S. Garner, *ibid.*, *2*, 414 (1963).

(8) L. P. Quinn and C. S. Garner, *ibid.*, *3*, 1348 (1964).

(9) J. M. Veigel and C. S. Garner, *ibid.*, *4*, 1569 (1965).

Although the primary aquation reaction has proved readily amenable to study, the secondary aquation is very complex and its detailed interpretation somewhat uncertain.

Experimental Section

cis-α-*Dichlorotriethylenetetraminechromium (III) Perchlorate.* This compound was prepared and characterized as described earlier.[2]

cis-β- or cis-β'-*Chloroaquotriethylenetetraminechromium(III) Cation.* This new complex was isolated in solution by cation-exchange chromatography from *cis-α*-[Cr(trien)Cl_2]ClO_4 reaction solutions. Typically, *ca.* 0.2 g of the latter compound was dissolved in 80 ml of 0.1 *F* $HClO_4$ and aquated in the dark usually for 1-2 hr at 20-25° (otherwise for 1 hr at 35°), then the solution was charged on to an 8-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100-200 mesh) at 1°. Unreacted purple dichloro complex and free Cl^- were eluted with *ca.* 150 ml of 1 *F* $HClO_4$, then the cloroaquo species (red band) was eluted with *ca.* 180 ml of 3 *F* $HClO_4$. In later preparations, especially where the reaction solution was to be examined for secondary aquation products, 6-12-cm × 1-cm diameter columns of H^+ Dowex AG50W-X4 resin (200-400 mesh) were used at 1°, with elution of unreacted dichloro complex with *ca.* 200 ml of 0.6 *F* $HClO_4$, followed by elution of the desired chloraquo species with *ca.* 150 ml of 1 *F* $HClO_4$. Center cuts of pink chloroaquo effluents were taken when high purity of the chloroaquo species was required. The solutions were usually *ca.* 1 m*F* in the complex. Attemps to isolate solid salts were unsucessful.

Diaquotriethylenetetraminechromium (III) Cation. A small excess of $NaNO_2$ was added to a solution of *cis-α*-[Cr(trien)$(N_3)_2$]Br[2] in 0.1 *F* $HClO_4$; the solution was charged on to a column of H^+ Dowex AG50W-X4 cation-exchange resin (200-400 mesh), the excess NO_2^- washed out with at least 200 ml of 0.1 *F* $HClO_4$, then the diaquo complex (apparently *cis-α* or *cis-β*) eluted with 100 ml of 3 *F* $HClO_4$ as an orange solution *ca.* 1 m*F* in the complex. An orange band of unidentified species was left on the column even after elution with 6 *F* $HClO_4$.

Other Chemicals. All other chemicals were C.p. or reagent grade. The water was doubly distilled, then passed through a mixed-bed cation-anion exchange resin and monitored for purity by electrical conductivity. All exchange resins were thoroughly washed with suitable aqueous solutions until color «throw» was negligible as measured spectrophotometrically.

Chemical Analyses. Solids and certain solutions were analyzed for Cr, Cl and in some cases for C and H also, as described earlier.[2] Most of the C and H analyses were made by Miss Heather King.

Chromatography of Hydrolyzed Solutions. Solutions of *cis-α*-Cr(trien)Cl_2^+ or of Cr(trien)$(OH_2)Cl^{2+}$ which had been allowed to hydrolyze under various conditions were examined for product composition by ion-exchange chromatography. In most cases the second of the two procedures mentioned above under the isolation of Cr(trien)$(OH_2)Cl^{2+}$ was used to determine the amounts of the dichloro and chloroaquo complexes present in hydrolyzed solutions. Following elution of the chloroaquo species, *ca.* 150-200 ml of 2 *F* $HClO_4$ was used to elute a purple product tentatively identified as one or more isomers of Cr(trienH)$(OH_2)_2Cl^{3+}$, and then *ca.* 100-200 ml of 3 *F* $HClO_4$ was employed to elute an orange species which appears to be one or more isomers of the diaquo complex, Cr(trien)$(OH_2)_2^{3+}$ (see Results). In some cases an unidentified orange effluent was then obtained by elution with 6 *F* $HClO_4$, and in some cases an orange to gray band remained on the column. Although the various bands generally appeared to be reasonably well separated by the above chromatographic procedure, spectral and Cl:Cr atom-ratio evidence indicated that the separations of the 2+ and 3+ species were not usually quantitative.

Kinetic Runs. Aquation of cis-α-Cr(trien)Cl_2^+ was followed spectrophotometrically, by titration of Cl^- released, and by chromatographic isolation of unreacted dichloro complex. Weighed samples (15-40 mg) of the perchlorate salt were dissolved in 50.00 ml of $HClO_4$-$NaClO_4$ solution of the desired concentrations and quickly brought to reaction temperature. For the spectrophotometric runs, the reaction was carried out in a 10.00-cm silica cell in a Cary Model 11 or 15 recording spectrophotometer with the cell thermostated at 35.00 ± 0.04, 25.00 ± 0.03, or 15.80 ± 0.03°; a matching silica cell filled with water was used as a reference. Spectral scans over the range700-340 mμ were made at known time intervals to search for isosbestic points and to give data for kinetic analysis. The first scan (taken as zero time) was taken 4-5 min after the cell was placed in the thermostated cell holder. In two runs (fourth and eighth in Table II) the spectrophotometer was set at 580 mμ and the chart run continuously at this fixed wavelength. Light was excluded as a routine precaution against possible photolysis, except during scans. For the Cl^- release runs, solutions prepared as above were placed in Al-foil-covered flasks in baths thermostated at 25.00±0.04 or 4.86±0.01°, and 2.00-ml aliquots taken at known time intervals and each quenched by delivery into an iced mixture of 23.0 ml of purified water and 75.0 ml of an acetone-detergent solution; the free Cl^- was potentiometrically titrated at 0° with 1.00 m*F* $AgNO_3$ within 5 min.[10] A blank solution without the complex was titrated in each run to correct for Cl^- impurities in the chemicals and water involved. In the chromatographic runs, unreacted *cis-α*-Cr(trien)Cl_2^+ was isolated chromatographically (see above) as a function of time.

The hydrolysis of chromatographically isolated Cr(trien)$(OH_2)Cl^{2+}$ and «purple product» (Cr(trienH)$(OH_2)_2Cl^{3+}$?) was similarly followed, but under a more limited range of conditions. Growth of the diaquo complex from the chloroaquo complex was studied chromatographically, and the change in visible absorption spectrum of the isolated diaquo species with time examined. Release of Cl^- by the «purple product» was examined by the method above.

Results

New Complexes and Their Spectra. Figure 2 exhibits the near-ultraviolet and visible absorption spectra of *cis-α*-Cr(trien)Cl_2^+ and the new complex

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[10] D. J. MacDonald and C. S. Garner, *J. Inorg. Nuclear Chem.*, *18*, 219 (1961).

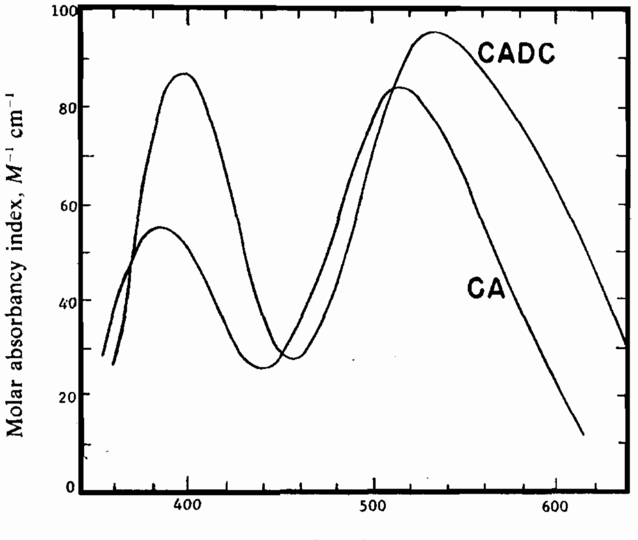

Figure 2. Visible absorption spectra of chromium(III) trien complexes at 20-25°: CADC, *cis*-α-[Cr(trien)Cl$_2$]ClO$_4$ in 0.1 *F* HClO$_4$; CA, *cis*-β- or *cis*-β′-Cr(trien)(OH$_2$)Cl^{2+} in 1.5 *F* HClO$_4$; the molar absorbancy index a_M (extinction coefficient ε) is defined by the relation $A = \log (I_0/I) = a_M cd$, where *c* is the molarity of the absorbing complex and *d* is the optical path in cm.

Cr(trien)(OH$_2$)Cl^{2+}, probably the *cis*-β or *cis*-β′ isomer (see Figure 1b, 1c and below). Values of the absorption maxima and minima of these two complexes and of unknown isomers of the purple species tentatively identified as Cr(trienH)(OH$_2$)$_2$Cl^{3+} and the orange species identified as Cr(trien)(OH$_2$)$_2^{3+}$ are given in Table I, together with values for related complexes.

Pink Cr(trien)(OH$_2$)Cl^{2+} chromatographically isolated from aquated *cis*-α-Cr(trien)Cl$_2^+$ solutions exhibits Cl:Cr atom ratios of 0.993-1.12 (most values *ca.* 1.01), has a chromatographic behavior expected for a doubly charged cation of its size, its growth curve from the dichloro parent shows it to be a directly formed product (or an isomer rapidly produced from the directly formed product), and the d-d bands move to shorter wavelengths on its formation as expected for replacement of ligand Cl by ligand H$_2$O, so the pink complex is clearly a chloroaquotriethylenetetraminechromium(III) species. Table I shows the visible absorption spectrum of the new chloroaquo complex to be very similar to the spectra of *cis*-Cr(en)$_2$(OH$_2$)Cl^{2+} and (with due regard for the Cr(III)-Co(III) shift) *cis*-β-Co(trien)(OH$_2$)Cl^{2+}, both of which have the same *cis*-MN$_4$(OH$_2$)Cl chromophore (M = Cr or Co), but the spectrum is very different from the spectrum of *trans*-Cr(en)$_2$(OH$_2$)Cl^{2+}. This rules out the possibility that this Cr(trien)(OH$_2$)Cl^{2+} is the *trans* isomer, but allows assignment to either a *cis*-α, *cis*-β or *cis*-β′ configuration. Hydrolysis rate considerations (see Discussion) make a *cis*-α assignment improbable, so we believe the complex has either the *cis*-β or *cis*-β′ geometry.

The orange species obtained from the action of excess NaNO$_2$ on *cis*-α-Cr(trien)(N$_3$)$_2^+$ would be expected to be *cis*-α-Cr(trien)(OH$_2$)$_2^{3+}$, assuming no isomerization. The color and chromatographic behavior are those expected for Cr(trien)(OH$_2$)$_2^{3+}$. The spectrum is similar to the spectra of *cis*-Cr(en)$_2$(OH$_2$)$_2^{3+}$ and either *cis*-α- or *cis*-β-Co(trien)(OH$_2$)$_2^{3+}$, but different from that of *trans*-Cr(en)$_2$(OH$_2$)$_2^{3+}$ (Table I), suggesting the Cr(trien)(OH$_2$)$_2^{3+}$ obtained from the azido complex is the *cis*-α or *cis*-β isomer (or a mixture of these two).

Chromatography of hydrolyzed *cis*-β- or *cis*-β′-Cr(trien)(OH$_2$)Cl^{2+} showed that the same, or a similar, form of Cr(trien)(OH$_2$)$_2^{3+}$ grows in the reaction solution with the same rate as free Cl$^-$ is produced, at least during the early stages of reaction. The chromatographically isolated diaquo effluents had an average spectrum as indicated in Table I and Cl:Cr atom ratios of 0.093-0.365 (usually *ca.* 0.2). The fact that Cl:Cr ratios are variable and higher than the expected value of zero presumably implies that small amounts of the 3+ purple product below (Cl:Cr = 1.0) are eluted

Table I. Absorption Maxima and Minima in the 340-700-mμ Range for Some Cr(III)-bis(en) and M(III)-trien (M = Co or Cr) Complexes at 20-25°[a]

Complex	λ_{max}, mμ	λ_{min}, mμ	λ_{max}, mμ	λ_{max}, mμ
cis-α-Cr(trien)Cl$_2^+$[b,c]	396 (86.7)	455 (28.5)	535 (95.5)	580 (79)sh[d]
cis-Cr(en)$_2$Cl$_2^+$[e]	402 (68.5)	456 (20.7)	528 (70.6)	
cis-α-Co(trien)Cl$_2^+$[f]	381 (132)sh[d]	~463 (45)	539 (132)	~600 (115)sh[d]
cis-β-Co(trien)Cl$_2^+$[f]	392 (118)sh[d]	~460 (47)	531 (131)	
trans-Co(trien)Cl$_2^+$[g]	~360 (62)		~455 (137)	630 (50)
cis-β- or *cis*-β′-Cr(trien)(OH$_2$)Cl^{2+}[c]	385 (56.2)	440 (25.7)	515 (83.5)	
cis-Cr(en)$_2$(OH$_2$)Cl^{2+}[e]	385 (55.7)	438 (20.3)	510 (71.4)	
trans-Cr(en)$_2$(OH$_2$)Cl^{2+}[e]	380 (45.4)	428 (23.7)	448 (24.4)	546 (20.5)
cis-α-Co(trien)(OH$_2$)Cl^{2+}[g]	~380 (100)	~445 (15)	~530 (125)	
cis-β-Co(trien)(OH$_2$)Cl^{2+}[g]	~370 (100)	~425 (30)	~510 (125)	
orange Cr(trien)(OH$_2$)$_2^{3+}$?[c,h]	~363	422	495	
orange Cr(trien)(OH$_2$)$_2^{3+}$?[c,i]	~372 (36)	~420 (22)	~497 (72)	
cis-Cr(en)$_2$(OH$_2$)$_2^{3+}$[j]	367 (42.5)	417 (17)	484 (67.0)	
trans-Cr(en)$_2$(OH$_2$)$_2^{3+}$[j]	361 (39.2)	404 (20.0)	442 (29.3)	508 (22.5)sh[d]
cis-α-Co(trien)(OH$_2$)$_2^{3+}$[g]	~355 (55)	~415 (20)	~500 (85)	
cis-β-Co(trien)(OH$_2$)$_2^{3+}$[g]	~360 (80)	~415 (20)	~495 (130)	
purple Cr(trienH)(OH$_2$)$_2$Cl^{3+}?[c,i]	~403 (32)	~450 (21)	~530 (49)	

[a] Usually 0.01-2 *F* HClO$_4$ solutions. Values inside parentheses are molar absorbancy indices in M^{-1} cm^{-1}. [b] Ref. 2. [c] This research. [d] Shoulder. [e] Ref. 5. [f] A. M. Sargeson, personal communication. [g] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, *4*, 45 (1965). [h] Prepared from azido complex. [i] Freshly chromatographed from hydrolyzed Cr(trien)(OH$_2$)Cl^{2+} solutions. [j] F. Woldbye, *Acta Chem. Scand.*, 12, 1079 (1958).

along with the orange diaquo species. Thus it is not clear whether this diaquo species is isomerically the same as that from the azido complex or not. At least it is clear from Table I that no appreciable fraction of the diaquo complex is the *trans* isomer.

Chromatography of hydrolyzed *cis*-β- or *cis*-β′-Cr (trien)$(OH_2)Cl^{2+}$ also revealed that a purple product, with Cl: Cr atom ratios of 0.954, 0.956 and 1.10, grows in the reaction solution at a rate only slightly smaller than for generation of the orange diaquo complex. From the chromatographic behavior the purple product, which appears from the kinetic evidence presented later to be a mixture of two isomers, behaves like a 3+ species for its size. Its d-d bands (Table I) are shifted to longer wavelengths, relative to the parent *cis*-β- or *cis*-β′-Cr(trien)$(OH_2)Cl^{2+}$, corresponding to replacement of a Cr-N bond (probably to a primary amino group of trien) by a Cr-O bond from an entering H_2O ligand. Thus all the evidence suggests that the purple product is a mixture of isomers of Cr(trienH)$(OH_2)_2Cl^{3+}$, in which the free end of the trien ligand has taken up a proton. This latter assumption is not certain, for slow proton uptake by amino groups is not unknown; however, if the purple product were Cr(trien-)$(OH_2)_2Cl^{2+}$ we would expect it to chromatograph at least partly into the Cr(trien)$(OH_2)Cl^{2+}$ fraction, whereas this is not observed and some tendency for the purple product to coelute with Cr(trien)$(OH_2)_2^{3+}$ is found instead.

Aquation of cis-α-*Cr(trien)*Cl_2^+. Table II presents the first-order rate constants k_1 defined by the rate law

$$-d(\textit{cis}\text{-}\alpha\text{-Cr(trien)Cl}_2^+)/dt = k_1(\textit{cis}\text{-}\alpha\text{-Cr(trien)Cl}^{2+}) \quad (1)$$

In the present spectrophotometric method k_1 was evaluated for each kinetic run by the relation

$$2.303 \log [(A_0 - A_\infty)/(A - A_\infty)] = k_1 t \quad (2)$$

where A_0, A and A_∞ are the optical absorbancies, at a given wavelength, at reaction time zero, time t and 100% aquation of one chloro ligand, respectively. With A_∞ calculated from the spectrum of *cis*-β- or *cis*-β′-Cr(trien)$(OH_2)Cl^{2+}$, plots of equation 2 at 400, 560 and 580 mμ generally gave good straight lines up to 35-50% reaction, with k_1 values at these wavelengths agreeing within *ca.* 5%. In the Cl^- release method k_1 was determined with the relation

$$2.303 \log [(V_\infty - V_0)/(V_\infty - V)] = k_1 t \quad (3)$$

where V_0, V and V_∞ are the volumes of $AgNO_3$ titrant for a standard aliquot (see Experimental Section) at reaction time zero, time t and for complete release of one chloro ligand, respectively; plots of equation 3 were linear to *ca.* 20-30% reaction. In the chromatographic method, plots of

$$2.303 \log (C_0/C) = k_1 t \quad (4)$$

where C_0 and C are, respectively, the concentrations of *cis*-α-Cr(trien)Cl_2^+ initially and at time t, were linear to 3 and 1.6 half-lives at 35° and 25°, respectively. A series of rate plots for four runs is displayed in Figure 3.

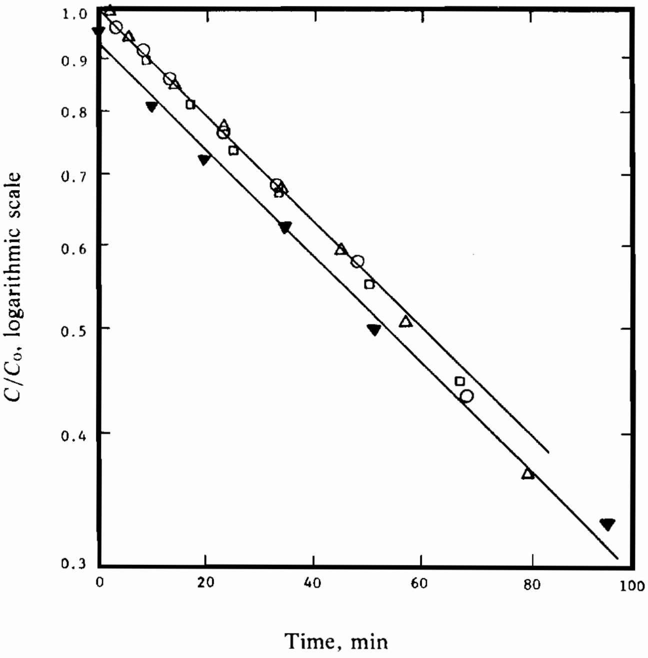

Figure 3. First-order rate plots of aquation of *cis*-α-dichlorotriethylenetetraminechromium(III) cation in 0.10 *F* $HClO_4$ (μ = 0.10 *M*) at 25.00°: ○, spectrophotometric method at 400 mμ; □, spectrophotometric method at 580 mμ; △, Cl^- release method; ▼, chromatographic isolation of unreacted *cis*-α-Cr(trien)Cl_2^+.

Table II. First-Order Rate Constants for Aquation of *cis*-α-Cr(trien)Cl_2^+ in the Dark

Method[a]	Temp., °C	$(HClO_4)$, *F*	C_0, m*F*	μ, *M*[b]	10^5k_1, sec^{-1}[c]
Spectro.	35.00	2.0	1.06	2.0	42.0 ± 3.0
Chrom.	35.00	0.10	1.3	0.10	64.5 ± 4.0
Spectro.	25.00	3.0	1.11	3.0	14.4 ± 0.6
Spectro.	25.00	0.10	0.97	3.0	14.4 ± 0.6
Spectro.	25.00	0.10	2.14	0.10	19.6 ± 0.8
Spectro.	25.00	0.10	0.98	0.10	18.9 ± 0.8
Spectro.	25.00	0.10	0.85	0.10	19.1 ± 0.8
Cl^-	25.00	0.10	2.07	0.10	19.2 ± 0.8
Chrom.	25.00	0.10	1.3	0.10	19.6 ± 1.4
Spectro.	25.00	0.0010	1.51	0.10	19.1 ± 0.8
Spectro.	15.80	0.10	1.08	0.10	6.42 ± 0.26
Cl^-	4.86	0.10	1.20	0.10	1.44 ± 0.06

[a] *Spectro.* = spectrophotometric determination at 400 mμ (except fourth and eighth runs at 580 mμ); Cl^- = titration of released Cl^-; Chrom. = chromatographic isolation of unreacted *cis*-α-Cr(trien)Cl_2^+. [b] Ionic strength, controlled with $NaClO_4$. [c] Errors are estimated standard deviations.

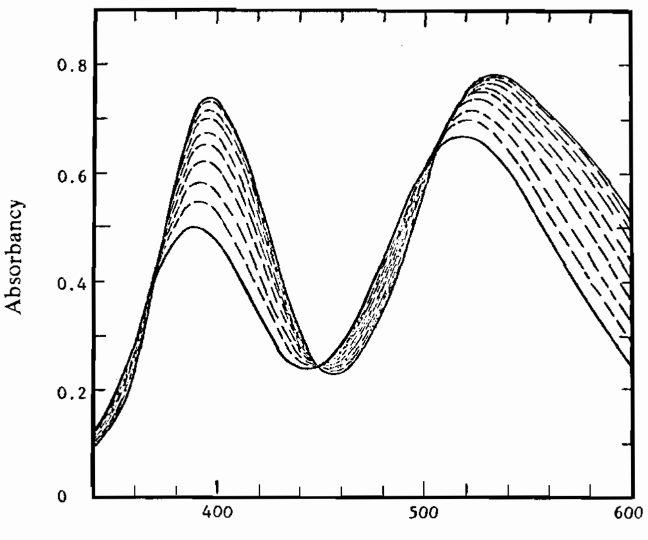

Figure 4. Change in absorption spectrum during aquation of *cis*-α-Cr(trien)Cl_2^+ in 0.10 *F* $HClO_4$ at 25.00°: reading downward at 535 mμ, reaction time is 2, 5, 10, 15, 25, 35, 50, 70, 90, 121 min, respectively.

Hydrolysis of cis-β- *or* cis-β'-*Cr(trien)*$(OH_2)Cl^{2+}$. Because of nonquantitative chromatographic separations of the chloroaquo complex and its hydrolysis products, the kinetics data exhibit considerable scatter and occasionally conflicting results. Part of this difficulty may have been a result of necessarily lengthy chromatographic elutions (up to 6 hrs) and resulting partial decomposition despite the use of columns at 1° to slow down the reactions. In fact, it was such variability that deterred us from a more thorough study of this system.

At 35.00° in 2.0 *F* $HClO_4$ chromatographic isolation of unreacted chloroaquo complex gave data which were treated by equation 4 (with k_1 replaced by k_4, and C_0 and C redefined in terms of chloroaquo complex) to give a series of first-order plots with appreciable scatter and half-lives from 30 to 40 min. We take a weighted average of 35 min, corresponding to a total first-order constant of $k_4 = 33 \times 10^{-5}$ sec^{-1} for the disappearance of *cis*-β- or *cis*-β'-Cr(trien)$(OH_2)Cl^{2+}$ by all paths. Only one run was made at low acidity, namely at 35.00° in 1.0 *F* $HClO_4$, for which $k_3 \approx 58 \times 10^{-4}$ sec^{-1}, suggesting that the chloroaquo complex may be disappearing as a result of both aquation and base hydrolysis or that ionic strength affects the rate. In all chromatographic experiments at 35°, no chloroaquo complex could be detected after 5 hr.

Plots of equation 3 (with k_4' replacing k_1) for Cl^- release by Cr(trien)$(OH_2)Cl^{+2}$ gave complex rate plots which were compatible with 50-65% of the chloroaquo complex disappearing in 2-3 *F* $HClO_4$ by a path involving Cl^- release with a half-life of 41-54 min at 35.00° and *ca.* 4 hr at 25.00°. In addition, at longer reaction times the rate plots were suggestive of the presence of two (or possibly three) components involving Cl^- release with half-lives of *ca.* 100-400 hr at 35.00° and *ca.* 600 hr at 25.00°. These long-lived Cl^--release species are probably associated with Cl^- release by the «purple-product» species (see below).

Attempts to establish the rates of formation of reaction products of the chloroaquo hydrolysis gave scattered results. At 35.00° in 2 *F* $HClO_4$ at short reaction times, it is clear that the orange diaquo and the «purple-product» species are growing in the reaction solution as the chloroaquo complex reacts. The amount of diaquo species appears to remain constant from 5 hr to at least 200 hr (chloroaquo parent no longer detectible), whereas the amount of «purple product» seems to decrease *ca.* 20% in this interval, relatively rapidly at first, then more slowly.

Hydrolysis of «Purple Product». One Cl^--release run was made on chromatographically isolated «purple product» in 2 *F* $HClO_4$ at 35.00°. The rate plot was complex, but could be resolved into two components with half-lives of 30-60 hr and 200-100 hr, present at $t = 0$ in approximately equal amounts. During the first 0.5-1 hr considerable change in the visible absorption spectrum occurred, with the d-d bands moving to longer wavelengths characteristic of Cr-N bond breakage and uptake of ligand H_2O, which we associate with one of the «purple-product» species forming Cr$(trienH_2)(OH_2)_3Cl^{4+}$.

Discussion

Aquation of cis-α-*Cr(trien)*Cl_2^+. From the spectral scans made (see Figure 4 for one of the runs) three well-defined isosbestic points are observed in the early stages of aquation of *cis*-α-Cr(trien)Cl_2^+. In ionic strength 0.1 *M*, these are at 370 ± 2 (48.7 ± 0.7), 449 ± 2 (29.1 ± 0.4) and 511 ± 4 mμ (83.0 ± 0.7),[11] which compare favorably with the values predicted from Figure 2 for the reaction

$$\textit{cis}\text{-}\alpha\text{-Cr(trien)Cl}_2^+ + H_2O =$$
$$= \textit{cis}\text{-}\beta\text{- or } \textit{cis}\text{-}\beta'\text{-Cr(trien)(OH}_2\text{)Cl}^{2+} + Cl^- \qquad (5)$$

namely, 370 ± 2 (48.0 ± 0.7), 450 ± 2 (28.5 ± 0.2) and 511 ± 4 mμ (83.0 ± 0.8); at ionic strength 3 *M* the experimental isosbestic points are essentially unaltered except for the 511-mμ point, which increases in molar absorbancy index to 89 ± 1 M^{-1} cm^{-1}. These isosbestic points, together with the good agreement among the values of k_1 obtained spectrophotometrically, by Cl^- release, and by chromatography (see Table II), means that there are no kinetically significant side reactions.

The data of Table II show that k_1 at 25° is essentially independent of H^+ concentration between 0.001 and 0.1 *M* at ionic strength 0.1 *M* and between 0.1 and 3 *M* at ionic strength 3 *M*. Therefore the reaction is aquation, with negligible contribution from base hydrolysis, as would be expected by analogy with *cis*-Cr$(en)_2Cl_2^+$. There is a decrease of *ca.* 25% in k_1 on increasing ionic strength with $NaClO_4$ from 0.1 to 3 *M*, which effect is not abnormal for such high ionic strengths.

Returning to equation 5, the observations may appear to be compatible also with a scheme in which *cis*-α-Cr(trien)Cl_2^+ isomerizes to the *cis*-β form in a rate-controlling step, with the *cis*-β-Cr(trien)Cl_2^+ then much more rapidly aquating to the observed product. This pathway seems very unlikely, since unsucessful attempts were made by House and Garner[2] to isomerize

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(11) Values inside the parentheses are molar absorbancy indices in M^{-1} cm^{-1}.

cis-α-Cr(trien)Cl_2^+ to the *cis*-β form by treatment with NaOH, followed by addition of excess 12 *F* HCl and storage overnight in a refrigerator, a procedure which quantitatively converts *cis*-α-Co(trien)Cl_2^+ to the *cis*-β isomer.[12] Moreover, *cis*-α-Co(trien)Cl_2^+ has been reported[13] as aquating 100% to *cis*-α-Co(trien)(OH_2)Cl^{2+} with retention of optical configuration. We suspect, therefore, that *cis*-α-Cr(trien)Cl_2^+ aquates 100% to *cis*-α-Cr(trien)(OH_2)Cl^{2+} and that k_1 is the rate constant for that aquation, and that the *cis*-α-chloroaquo ion rapidly (on the scale involved) isomerizes to the apparently observed *cis*-β- or *cis*-β′-Cr(trien)(OH_2)Cl^{2+}. That this isomerization be relatively rapid is required by the good isosbestic points found in aquation of *cis*-α-Cr(trien)Cl_2^+ (spectral analogy with the Co(III) analogs suggests *cis*-α- and *cis*-β-Cr(trien)(OH_2)Cl^{2+} would have similar spectra, but definitely different enough to destroy the isosbestic points found) and by the fact that the spectra of Cr(trien)(OH_2)Cl^{2+} chromatographically isolated from its hydrolysis solutions in 2 *F* $HClO_4$ at 35° at *ca.* 10 min and at 30 min were the same.

A scheme which would also appear at first thought to be compatible with the observations would be one in which the directly formed product is *cis*-α-Cr(trien)(OH_2)Cl^{2+}, which then directly hydrolyzes. This scheme is very improbable because analogy with the Co(III) system[13] implies that *cis*-α-Cr(trien)(OH_2)Cl^{2+} would aquate too slowly by a factor of *ca.* 100 to account for the observed rate of Cl^- release; indeed our supposition that it is the *cis*-β or *cis*-β′ isomer of the chloroaquo complex which is hydrolyzing here is further supported by the fact that the rate of Cl^- release is about what would be expected by analogy with *cis*-β- or *cis*-β′-Co(trien)(OH_2)Cl^{2+} (see Table III below).

In 0.1 *F* $HClO_4$ (μ = 0.1 *M*) we take for 10^5k_{13} (assumed equal to 10^5k_1, and related to other rate constants in Figure 6) 65 ± 4 at 35.00°, 19.2 ± 0.6 at 25.00°, 6.4 ± 0.3 at 15.80° and 1.44 ± 0.06 sec^{-1} at 4.86°. These four values give an excellent Arrhenius plot, from which we obtain $E_a = 21.2 \pm 0.7$ kcal $mole^{-1}$, log *PZ* = 11.8 ± 0.5 (sec^{-1}) and $\Delta S°_{298}{}^* = -6.4 \pm 2.3$ cal deg^{-1} $mole^{-1}$.

Hydrolysis Reaction Scheme. It is useful at this point to construct a reaction scheme to relate all the rate observations at 35.00° in 2 *F* $HClO_4$ (Figure 5).

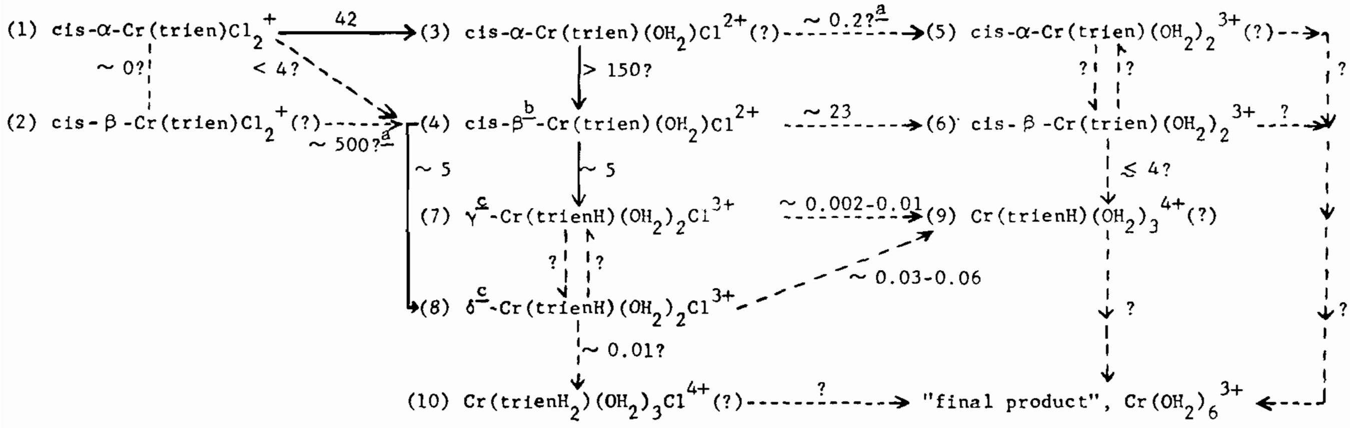

Figure 5. Rate constants (10^5k, sec^{-1}) for aquation (dichloro complexes), hydrolysis (other complexes) and isomerization reactions in 2 *F* $HClO_4$ at 35° in the absence of light. [a] Estimated from Co(III) analog in 0.01 *F* $HClO_4$. [b] Or *cis*-β′-. [c] Unknown isomers. ? = an estimate, or no proof complex of this formula exists.

Hydrolysis of *cis*-β- or *cis*-β′-Cr(trien)(OH_2)Cl^{2+} to Cr(trien)$(OH_2)_2^{3+}$ (probably *cis*-β) and two different isomeric forms (λ and δ, Figure 5) of Cr(trienH)$(OH_2)_2Cl^{3+}$ concurrently accounts for the observed growth of these species from their chloroaquo parent, and is compatible with the complex rate plots for Cl^- release observed in solutions of the chloroaquo parent over long time periods. Moreover it accounts for the spectral changes during this hydrolysis in that the d-d bands show a pronounced drop in intensity but only slight changes in wavelengths until long reaction periods, when they move to longer wavelengths; at the shorter reaction times this behavior is expected, for the hydrolysis to Cr(trien)$(OH_2)_2^{3+}$ would shift the bands to lower wavelengths but the simultaneous hydrolysis to Cr(trienH)$(OH_2)_2Cl^{3+}$ would counterbalance at least approximately this wavelength shift. Species 10 is included to account somewhat better for the observed complex Cl^- release observations and for observed spectral changes in isolated «purple product», for the apparent hold up of some Cl^--containing species on the chromatographic columns following elution of Cr(trien)$(OH_2)_2^{3+}$ with 3 *F* $HClO_4$ and, together with species 9, for the appearance of apparently 4+ charged species on the columns at fairly early reaction times. Hydrolysis of orange Cr(trien)$(OH_2)_2^{3+}$ to a hypothesized Cr(trienH)$(OH_2)_3^{4+}$ is included in Figure 5 to account for moderately fast spectral changes observed in chromatographically isolated orange diaquo complex, in which the d-d bands moved to longer wavelength as expected for Cr-N bond breakage with uptake of ligand H_2O.

In a single experiment with *cis*-α-[Cr(trien)Cl_2]ClO_4 aged 20 days in 0.1 *F* $HClO_4$ at 60° the visible absorption spectrum changed to that of $Cr(OH_2)_6^{3+}$ except for a minor difference in band intensities. Evidently the trien ligand, which we postulate is hydrolyzed in discrete steps of one Cr-N bond broken at a time, is finally removed completely with little or no diversion of Cr(III) into polymeric species.

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(12) D. A. Buckingham and D. Jones, *Inorg. Chem.*, *4*, 1387 (1965).
(13) A. M. Sargeson and G. H. Searle, *Nature*, *200*, 356 (1963).

Comparison with Cr(III)-bis(en) and Co(III)-trien Complexes. The most direct comparison with the complicated Cr(en)$_2$Cl$_2^+$ — Cr(en)$_2$(OH$_2$)Cl^{2+} system is made by referral to Figure 1 of reference 6, although the rate data in that figure are for reactions in 0.1 *F* HNO$_3$. Table III records specific rate comparisons with related Cr(III)-bis(en) and Co(III)-trien complexes.

Table III. Comparison of Aquation Rates of Cr(III)-trien Complexes with Cr(III)-bis(en) and Co(III)-trien Complexes

Complex	Temp., °C	(HClO$_4$), *F*	μ,[a] *M*	10^5k sec^{-1}	E_a, kcal	$\Delta S°_{298}$, cal deg^{-1}
cis-α-Cr(trien)Cl$_2^+$[b]	25	0.10	0.10	19.2	21.2	—6.4
cis-Cr(en)$_2$Cl$_2^+$[c]	25	0.10	0.11	33.0	21.1	—5.7
cis-α-Co(trien)Cl$_2^+$[d]	25	0.01	0.01	16		
cis-β-Co(trien)Cl$_2^+$[d]	25	0.01	0.01	150		
trans-Co(trien)Cl$_2^+$[d]	25	0.01	0.01	350		
cis-β[e]-Cr(trien)(OH$_2$)Cl^{2+}[b, f, g]	25	2	2	~5		
cis-Cr(en)$_2$(OH$_2$)Cl^{2+}[g, h]	25	0.10[i]	0.10	2.6		
cis-α-Co(trien)(OH$_2$)Cl^{2+}[g, j]	25	0.01	0.1	~0.06		
cis-β-Co(trien)(OH$_2$)Cl^{2+}[d, g]	25	0.01	0.01	2.4		
cis-β′-Co(trien)(OH$_2$)Cl^{2+}[d, g]	25	0.01	0.01	8.0		

[a] Ionic strength, usually controlled with NaClO$_4$. [b] This research. [c] J. Selbin and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 79, 4285 (1957). [d] Ref. 13. [e] Or *cis*-β′. [f] Cl$^-$ release path only. [g] Rate constant may possibly include an unknown contribution from base hdrolysis. [h] Estimated from 35°*k* of Ref. 6. [i] HNO$_3$. [j] Estimated from 40° and 35°*k*, personal communication from A. M. Sargeson.

In general, there is considerable similarity of rates between the Cr(III) and Co(III) *cis*-α triethylenetetramine complexes, as would be expected by analogy with comparisons of the bis(ethylenediamine) complexes, except where reactions involving M-N bond breakage is involved. As was true for related systems of Cr(III) amine complexes[4-9], we again observe good evidence for Cr-N bond breakage in competition with Cr-Cl bond breakage, which now warrants our predicting that kinetic and stereochemical studies of Cr(III) amine systems are likely to be much more complex and difficult than for their Co(III) analogs.

Table III shows that *cis*-α-Cr(trien)Cl$_2^+$ aquates at 25° (μ = 0.1) at about 60% of the rate with which *cis*-Cr(en)$_2$Cl$_2^+$ aquates. This effect of chelating with a CH$_2$CH$_2$ bridge the two amino N atoms which are *cis* to each other in the ethylenediamine complex is in accord with earlier comparisons[14] of the chelation effect on aquation rates of similar complexes. As supported by Langford and Gray,[15] this chelation effect is probably a solvent effect in which the organic ligands tend to break up the solvation shell of the reactant complex; in passing to the transition state with separating charges, the complex needs greater solvation, but is presumably actually less well solvated with increasing organic chelation. With the chloroaquo species the effect appears to be in the opposite direction, but the 25° value for *cis*-β- or *cis*-β′-Cr(trien)(OH$_2$)Cl^{2+} is an extrapolation from 35° runs in quite different acidity and ionic strength, and we prefer not to attach much significance to the comparison with *cis*-Cr(en)$_2$(OH$_2$)Cl^{2+}; moreover the role of base hydrolysis in all of the chloroaquo complexes of Table III is unknown.

As we were writing this paper, a report[16] of the visible absorption spectrum of dichloro-1,4,8,11-tetraazaundecanechromium(III) cation and its qualitative change with time in aqueous solution came to our attention. This complex is related to *cis*-α-Cr(trien)Cl$_2^+$ by insertion of a methylene group between the third and fourth methylene groups of triethylenetetramine. Qualitatively, the spectrum and apparent aquation rate are similar to those of *cis*-α-Cr(trien)Cl$_2^+$.

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(14) See, e.g., R. G. Pearson, C. R. Boston and F. Basolo, *J. Phys. Chem.*, 59, 304 (1955).

(15) C. H. Langford and H. B. Gray, «Ligand Substitution Processes», W. A. Benjamin, Inc., New York, Amsterdam, 1965, p. 67.

(16) B. Bosnich, R. D. Gillard, E. D. McKenzie and G. A. Webb, *J. Chem. Soc.*, (A), 1331 (1966).