

Synthesis of a Monodentate Ethylenediamine Complex of Chromium(III) and Kinetics of Hydrolysis of Tetraaquoethylenediaminechromium(III) Cation and of Pentaquo(2-aminoethylammonium)chromium(III) Cation^{1a,b}

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The new complex $\text{Cr}(\text{enH})(\text{OH}_2)_5^{4+}$ has been synthesized from $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$ and isolated in aqueous solution; the visible absorption spectrum has been obtained. This is apparently the first isolation of a chromium(III) complex with a monodentate ethylenediamine ligand. The kinetics of hydrolysis of $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$ to $\text{Cr}(\text{enH})(\text{OH}_2)_5^{4+}$ and of aquation of the pentaquo complex to $\text{Cr}(\text{OH}_2)_6^{3+}$ in the dark have been studied spectrophotometrically in 0.03–3 *F* HClO_4 ($\mu = 0.15$ –3 *M*, NaClO_4) at 60, 80, 85, and 90°. At 59.90° the first-order rate constant k_1 for hydrolysis of $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$ in 3.0 *F* HClO_4 is $(3.0 \pm 0.2) \times 10^{-6} \text{ sec}^{-1}$, $E_a = 27.7 \pm 1.5 \text{ kcal mole}^{-1}$, and $\log PZ (\text{sec}^{-1}) = 13.7 \pm 1.1$; acid concentration and ionic strength dependencies are small. At 59.90° the first-order rate constant k_2 for aquation of $\text{Cr}(\text{enH})(\text{OH}_2)_5^{4+}$ to $\text{Cr}(\text{OH}_2)_6^{3+}$ in 3.0 *F* HClO_4 is $(1.9 \pm 0.3) \times 10^{-6} \text{ sec}^{-1}$, $E_a = 25.4 \pm 2.3 \text{ kcal mole}^{-1}$, and $\log PZ (\text{sec}^{-1}) = 10.9 \pm 1.5$; at 60–90°, k_2 is essentially independent of HClO_4 concentration from 0.03 to 3 *F* at $\mu = 3 \text{ M}$ and is independent of μ from 0.15 to 3 *M* in 0.1 *F* HClO_4 .

Introduction

The tetraaquoethylenediaminechromium(III) cation, $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$, has been hypothesized^{2,3} as an intermediate in the hydrolysis of *cis*-diaquobis(ethylenediamine)chromium(III) cation, *cis*- $\text{Cr}(\text{en})_2(\text{OH}_2)_2^{3+}$, in acid solution to hexaaquochromium(III) cation, $\text{Cr}(\text{OH}_2)_6^{3+}$, based on interpretation of the changes in the visible absorption spectrum of the reaction solution. A second intermediate hypothesized in the hydrolysis was described² as a complex in which one end of the ethylenediamine ligand became free, the vacated coordination site of the central chromium atom then becoming occupied by a water molecule. Neither intermediate was isolated, although attempts were made^{2,3} to deduce the visible absorption spectrum of the tetraaquo complex from the spectral data. An attempt was made to obtain rate constants for aquation of the tetraaquo and the monodentate ethylenediamine complexes² and the equilibrium constants for what were assumed to be equilibria involving the hexaaquo, tetraaquo, and diaquo complexes.³

In 1965, House and Garner^{4,5} synthesized tetraaquoethylenediaminechromium(III) cation by decomposition of diperoxaquoethylenediaminechromium(IV) monohydrate, $[\text{Cr}(\text{en})(\text{OH}_2)(\text{O}_2)_2] \cdot \text{H}_2\text{O}$, in 0.5–3 *F* perchloric acid and obtained the visible absorption spectrum. This was similar to the spectra hypothesized earlier^{2,3} but was sufficiently different to raise doubts of the validity of the kinetic and thermo-

dynamic interpretations referred to above. The availability of solutions of the pure tetraaquo complex prompted us to examine directly the kinetics of its hydrolysis and to attempt to isolate the intermediate in the conversion of the tetraaquo complex to the hexaaquo complex.

We report here the successful chromatographic isolation of the intermediate, pentaquo(2-aminoethylammonium)chromium(III) cation, $\text{Cr}(\text{enH})(\text{OH}_2)_5^{4+}$,⁶ in aqueous solution and its visible absorption spectrum. So far as we know, this is the first isolation of a complex of chromium(III) with a monodentate ethylenediamine ligand. We also report the results of our kinetic studies of the aquation of this intermediate to the hexaaquo complex and of the hydrolysis of the tetraaquo complex.

Experimental Section

Tetraaquoethylenediaminechromium(III) Cation.—The method of Hoffman,⁷ as modified by House and Garner,⁵ was used to prepare $[\text{Cr}(\text{en})(\text{OH}_2)(\text{O}_2)_2] \cdot \text{H}_2\text{O}$. The diperoxo compound, used fresh or after storage in the dark at 1–5° for up to 3 weeks, was converted to $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$ by a modification of the method given earlier.^{4,5} Ca. 1.9 g of $[\text{Cr}(\text{en})(\text{OH}_2)(\text{O}_2)_2] \cdot \text{H}_2\text{O}$ was dissolved in small portions (*caution*⁸) in 80 ml of 2 *F* HClO_4 (or sometimes 0.5 g in 50 ml of 1 *F* HClO_4) and heated at 50° for 2 hr with occasional stirring; then the pink-red solution was used fresh or stored up to 3 weeks in the dark at 1–5° before dilution at 0° with water, NaOH, and/or NaClO_4 solutions for kinetic runs in 1 *F* HClO_4 or lower acidity. For kinetic runs of acidity greater than 1 *F* HClO_4 , each $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$ solution was chromatographed as follows.⁹ Ca. 10 ml of $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$

(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-34P12-67 to the AEC. (b) Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March–April 1968. (c) National Science Foundation Undergraduate Summer Research Participant, 1965.

(2) H. L. Schläfer and R. Kollrack, *Z. Physik. Chem. (Frankfurt)*, **18**, 348 (1958).

(3) M. Ohta, H. Matsukawa, and R. Tsuchiya, *Bull. Chem. Soc. Japan*, **37**, 692 (1964).

(4) D. A. House and C. S. Garner, *Inorg. Nucl. Chem. Letters*, **1**, 137 (1965).

(5) D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 840 (1966).

(6) The abbreviation enH is used to denote a monodentate ethylenediamine ligand with its free N atom protonated: $-\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$.

(7) K. A. Hoffman, *Ber.*, **39**, 3181 (1906).

(8) The diperoxo compound is light sensitive and explodes at 96–97° if heated at 2°/min.⁵ Considerable effervescence occurs in the dissolution in HClO_4 . Shielding should be used as a precaution despite the fact that we have never had any difficulty with the procedure.

(9) In preliminary experiments with chromatographed and nonchromatographed $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$ small differences (up to $\pm 2 \text{ m}\mu$ and ca. 10% in molar absorptancy indices of the absorption bands) were observed in their visible absorption spectra, and chromatography was used subsequently where possible as a routine precaution to obtain pure $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$.

(ca. 0.1 *F* in complex and 1–2 *F* in HClO₄) was diluted with 10 ml of water and charged onto an 8-cm × 1-cm diameter column of H⁺ Dowex AG50W-X8 cation-exchange resin (100–200 mesh) operated at 20–25° with flow rates of ca. 5 ml/min. To remove any Cr(OH₂)₆³⁺ possibly present, 50 ml of 1.5 *F* HClO₄ was run through the column and discarded. Ca. 50 ml of 2 *F* HClO₄ was used next to bring the Cr(en)(OH₂)₄³⁺ to the bottom of the resin column. An additional 125 ml of 2 *F* HClO₄ eluted perhaps 75% of the Cr(en)(OH₂)₄³⁺; a center cut obtained after discarding the first 25 ml of effluent was used at once for kinetic runs, after adjustment of acidity and ionic strength. The visible absorption spectrum was recorded routinely as a purity check.

Pentaaquo(2-aminoethylammonium)chromium(III) Cation.—This complex was synthesized and isolated as follows. Non-chromatographed Cr(en)(OH₂)₆³⁺, prepared as above in 2 *F* HClO₄, was aged ca. 15 hr (ca. 2 half-lives) at 80° in the dark; 25 ml of the aged solution was diluted with 25 ml of water and charged onto a fresh cation-exchange column of the kind described above. Perhaps 80% of the Cr(OH₂)₆³⁺ produced (gray-blue band) was eluted with 50 ml of 1.5 *F* HClO₄, and 70–80 ml of 2 *F* HClO₄ was used to elute the rest of the Cr(OH₂)₆³⁺ and some unreacted Cr(en)(OH₂)₄³⁺. Then 20 ml of 3 *F* HClO₄ eluted the rest of the Cr(en)(OH₂)₄³⁺ (red band) and perhaps 10–20% of the intermediate (purple band, immediately above the red band without a gap between). An additional 100 ml of 3 *F* HClO₄ eluted the intermediate, typically as a purple solution ca. 6 *mF* in Cr(enH)(OH₂)₄⁴⁺ and free of other complexes. Purity was checked by routine recording of the visible absorption spectrum. These purple solutions were normally used in kinetic runs started the same day, with storage otherwise up to 2 days in the dark at 1–5°. For certain kinetic runs the acid concentration was adjusted by careful addition of NaOH at 0° or by use of the OH⁻ Dowex AG2-X8 technique at 0° described earlier.^{10,11}

To verify that the purple complex is an ethylenediamine complex, we rechromatographed a solution of the complex using 2 *F* H₂SO₄ in place of the 3 *F* HClO₄ eluent to free the complex from ClO₄⁻ (which interferes with the Kjeldahl method) and analyzed the resulting purple effluent for N and Cr.

Hexaquo chromium(III) Cation.—To obtain an accurate visible absorption spectrum of Cr(OH₂)₆³⁺ for isobestic point predictions, we prepared [Cr(OH₂)₆](ClO₄)₃·*x*H₂O by the method of Emerson and Graven¹² and then charged 20 ml of a solution 10 *mF* in this complex and 0.1 *F* in HClO₄ onto a cation-exchange column of the kind described above. Ca. 80 ml of 1 *F* HClO₄ moved the gray-blue band to the bottom of the resin column, 20 ml more was passed and discarded, and then the next 30 ml was collected for spectral recording and Cr analysis. The absorption maxima and minimum found in 0.1–3 *F* HClO₄ at 20–25° were at 407 (max, *a*_M 15.3), 478 (min, *a*_M 2.96), 573 (max, *a*_M 13.0), and 665 *mμ* (sh, *a*_M 2.1 *M*⁻¹ *cm*⁻¹), the same within experimental error as the values reported earlier by Elving and Zemel¹³ and by Plane and Hunt,¹⁴ and similar to the values of Emerson and Graven.¹²

Other Chemicals.—Other chemicals were CP or reagent grade, except NaClO₄, which was prepared by dissolution of reagent grade NaHCO₃ in a slight excess of CP HClO₄ with recrystallization twice from water. All water was doubly distilled, then passed through a mixed-bed cation-anion-exchange resin and monitored for purity by electrical conductivity.

Analytical Methods.—Chromium was determined by spectrophotometric analysis of CrO₄²⁻ at 372 *mμ* with a Beckman DU instrument after decomposition of the complexes and oxidation with hot alkaline peroxide. Nitrogen was determined by a micro-Kjeldahl method.

Kinetic Runs.—Solutions of Cr(en)(OH₂)₄³⁺ or of Cr(enH)(OH₂)₄⁴⁺ were sealed in Pyrex ampoules, wrapped in Al foil to exclude light, and brought to bath temperatures thermostated

to ±0.05°. For 60° runs, ampoules were put in the 60° bath, and “zero-time” absorbancy readings were taken 10–15 min later. For runs at 80–90°, the ampoules were agitated for 1–2 min in a hotter bath to bring them 1–5° below thermostated temperature; then they were put in the thermostated baths and “zero time” was taken 5 min later. Ampoules were removed at known times, quenched in ice, and then stored up to 2 days at 1–5° in the dark prior to recording the absorption spectra at 20–25° of all ampoules of a given run at one time to improve accuracy in locating isobestic points.

Some Cr(enH)(OH₂)₄⁴⁺ runs were initiated by allowing Cr(en)(OH₂)₄³⁺ solutions to react, following the optical absorbancy until appreciable fractions of the chromium were in the form of the intermediate, and then subjecting the data to computer analysis (see below).

Spectrophotometry.—Kinetic and molar absorbancy index spectra were recorded in 10.00-cm matched quartz cells with a Cary Model 11 or 15 spectrophotometer, with identical solutions, except for the complexes, in the reference cell.

Computer Programs.—Computer analysis of the Cr(en)(OH₂)₄³⁺ kinetic runs was required because of consecutive first-order kinetics with the primary and secondary hydrolysis rate constants, *k*₁ and *k*₂, in a ratio of only 2–4.

A program which fitted five variables (*k*₁, *k*₂, and the molar absorbancy indices *a*_{MA}, *a*_{MB}, and *a*_{MC}) of the tetraaquo, pentaaquo, and hexaquo complexes, respectively) to the experimental absorbancies *A* at times *t* (*C*₀ = molarity of Cr(en)(OH₂)₄³⁺ at *t* = 0; *d* = optical path in cm) with the equation

$$A/C_0d = a_{MA}e^{-k_1t} + a_{MB}k_1[(e^{-k_2t} - e^{-k_1t})/(k_1 - k_2)] + a_{MC}[1 + (k_2e^{-k_1t} - k_1e^{-k_2t})/(k_1 - k_2)] \quad (1)$$

was written in FORTRAN IVG for the IBM 360/75 computer of the UCLA Campus Computing Network. The program is a modified version of that of Wiberg,¹⁵ in which the output values of *k*₁ and *k*₂ from the normal Wiberg program are then varied by ±1% one at a time and used as new input, and if this reduces the average deviation, the whole procedure is recycled with the changed value of *k*₁ or *k*₂. This modification guards against false error minima being found.

Original input *k*₂ values were obtained by application of eq 3 (see Results) to solutions of chromatographically isolated Cr(enH)(OH₂)₄⁴⁺. These values of *k*₂, together with values of *k*₁ estimated from initial slopes of first-order rate plots for Cr(en)(OH₂)₄³⁺ hydrolysis, were introduced into a trial-and-error program written for an Olivetti-Underwood Programma 101 desktop computer, using eq 1 with omission of the term involving *a*_{MC}. The output *k*₁ values then became the input *k*₁ values for the “five-variable” IBM 360/75 computer program, together with the above *k*₂ values and the experimental values of the molar absorbancy indices at 510 *mμ*, the spectral region of greatest absorbancy change in the primary hydrolysis. Because of slow thermal equilibration near *t* = 0, the first three points of each run (ca. 10–20% reaction) were discarded.

Because the output *a*_{MB} value differed from the experimental value by more than the experimental error, the effect on the other output variables was studied with a “four-variable” computer program in which *a*_{MB} was held constant at its experimental value; the resulting changes in *k*₁ and *k*₂ were sufficiently small (see Results) to satisfy us that the “five-variable” program *k*₁ and *k*₂ values were compatible with the experimental molar absorbancy indices. In fact, a “two-variable” program, in which all molar absorbancy indices were held constant at the experimental values gave, except for one poor run, values of *k*₁ and *k*₂ with only 8 and 24% respective average deviations from the “five-variable” program values. The “five-variable” values are considered most reliable because they allow for reasonable deviations of the molar absorbancy indices from their experimental values. The experimental data are not sufficiently accurate to warrant use of a least-squares program using a Maclaurin expansion of eq 1.

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

(11) D. C. Olson and C. S. Garner, *ibid.*, **2**, 558 (1963).

(12) K. Emerson and W. M. Graven, *J. Inorg. Nucl. Chem.*, **11**, 309 (1959).

(13) P. J. Elving and B. Zemel, *J. Am. Chem. Soc.*, **79**, 1281 (1957).

(14) R. A. Plane and J. P. Hunt, *ibid.*, **79**, 3343 (1957).

(15) K. B. Wiberg, “Computer Programming for Chemists,” W. A. Benjamin, Inc., New York, N. Y., 1965, p 185.

As a final test of the "five-variable" program, an accurate, synthetically generated set of absorbancy data for a consecutive first-order kinetic sequence with reaction from $t = 0$ to 25% C and with $k_1 = 2k_2$ was fed into the computer. The results were as shown below. The ratios $a_{MA}:a_{MB}:a_{MC}$ are similar to those of the

	$10^4 k_1$	$10^4 k_2$	a_{MA}	a_{MB}	a_{MC}
Input	2.00	2.50	105	47.5	10.5
Output	1.06	4.94	100	52.5	10.4
Correct	1.00	5.00	100	50.0	10.0

experimental system studied, and since the input k_1 values in the actual runs were in general not off more than 50% from the output values, the above results attest to the reliability of the program for our data.

Results

Characterization of $\text{Cr}(\text{enH})(\text{OH}_2)_5^{4+}$.—This purple complex was characterized by its mode of formation (hydrolysis of $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$), by its aquation product ($\text{Cr}(\text{OH}_2)_6^{3+}$), by its N:Cr atom ratio (2.06), and by its chromatographic behavior (more difficultly eluted than $\text{Cr}(\text{OH}_2)_6^{3+}$ and $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$ and compatible with a 4+ charge). As expected for this complex, its visible absorption spectrum (Figure 1) exhibits d-d absorption bands at wavelengths intermediate to those of $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$ and $\text{Cr}(\text{OH}_2)_6^{3+}$. The absorption maxima are at 396 (a_M 21.5 $M^{-1} \text{ cm}^{-1}$) and 549 $m\mu$ (a_M 22.2 $M^{-1} \text{ cm}^{-1}$), with a shoulder at 666 $m\mu$ (a_M 1.4 $M^{-1} \text{ cm}^{-1}$) and a minimum at 462 $m\mu$ (a_M 5.70 $M^{-1} \text{ cm}^{-1}$). These absorption bands agree well with those reported by Ardon and Mayer¹⁶ for $\text{Cr}(\text{NH}_3)(\text{OH}_2)_5^{3+}$, namely, 397 (a_M 21.8 $M^{-1} \text{ cm}^{-1}$) and 545 $m\mu$ (a_M 22.1 $M^{-1} \text{ cm}^{-1}$), as expected since the two complexes have essentially the same chromophores and symmetry.

Schläfer and Kollrack² had postulated the intermediate in hydrolysis of $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$ to be $\text{Cr}(\text{en})(\text{OH}_2)_5^{3+}$, with the free end of the ethylenediamine ligand unprotonated (see Introduction). Although slow proton uptake by amino groups is not unknown, we believe the time scale here is adequate for proton uptake, which would tend to stabilize the pentaquo complex.¹⁷ Moreover, the 4+ charge we assume for the pentaquo complex is probably more in accord with the chromatographic behavior than a 3+ charge.

Aquation of $\text{Cr}(\text{enH})(\text{OH}_2)_5^{4+}$.—Table I gives the rate constants k_2 defined by the equation

$$-d(\text{Cr}(\text{enH})(\text{OH}_2)_5^{4+})/dt = k_2(\text{Cr}(\text{enH})(\text{OH}_2)_5^{4+}) \quad (2)$$

for the disappearance of $\text{Cr}(\text{enH})(\text{OH}_2)_5^{4+}$ in HClO_4 - NaClO_4 solutions of several acidities and ionic strengths, and initially free of other Cr(III) complexes, at 60, 80, 85, and 90°. These values of k_2 (designated by footnote *e* or *f*, Table I) were evaluated by the relation

$$\ln [(A_0 - A_\infty)/(A - A_\infty)] = k_2 t \quad (3)$$

where A_0 , A , and A_∞ are the optical absorbancies (at a given wavelength) at reaction time zero, time t , and at 100% aquation to $\text{Cr}(\text{OH}_2)_6^{3+}$, respectively. Rate

(16) M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962).

(17) E. Jørgensen and J. Bjerrum, *Acta Chem. Scand.*, **13**, 2075 (1959), have commented for the same reasons that another reaction intermediate postulated as $\text{Cr}(\text{en})_2(\text{en})\text{OH}_2^{3+}$ by H. L. Schäfer and O. Kling, *Z. Physik. Chem. (Frankfurt)*, **16**, 14 (1958), is probably $\text{Cr}(\text{en})_2(\text{enH})\text{OH}_2^{4+}$.

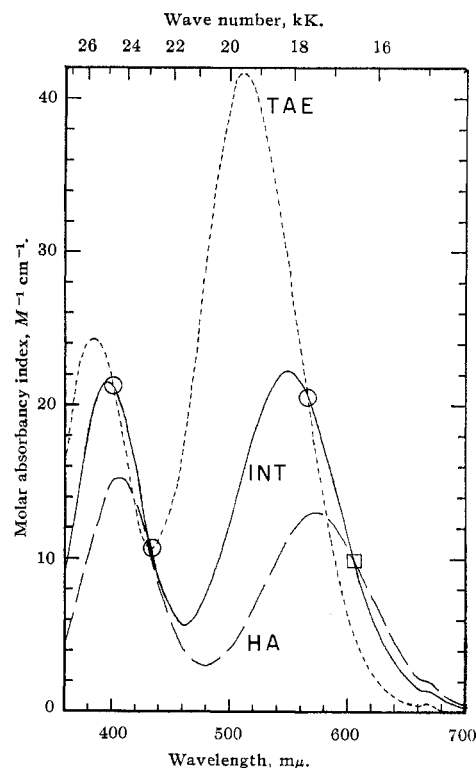


Figure 1.—Visible absorption spectra of some Cr(III) complexes in 0.1–3 *F* HClO_4 at 20–25°: TAE, $\text{Cr}(\text{en})(\text{OH}_2)_5^{4+}$; INT, $\text{Cr}(\text{enH})(\text{OH}_2)_5^{4+}$; HA, $\text{Cr}(\text{OH}_2)_6^{3+}$. The molar absorbancy index a_M (molar extinction coefficient ϵ) is defined by the relation $\log(I_0/I) = A = a_M c d$, where c is the molarity of the absorbing complex and d is the optical path in centimeters.

plots based on this relation generally gave good linearity as far as the runs were followed (to ca. 75% reaction). A significant contribution to the disappearance of the pentaquo ion from back reaction to $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$ is ruled out by the existence of sharp isosbestic points (see Discussion) and the observed first-order rate law.

Values of k_2 designated by footnote *b* in Table I were obtained from a "five-variable" computer program (see Experimental Section) applied to eq 1 and to absorbancy data from $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$ reaction solutions (initially ca. 100% $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$) in which the amount of $\text{Cr}(\text{OH}_2)_6^{3+}$ formed at the longest reaction time ranged from 4 to 95% (most typical, ca. 30%). In general, these values of k_2 agree with the directly determined values within the experimental errors, and no dependence of k_2 on the wavelength chosen for rate analysis is noted.

The "five-variable" program, however, gave an average output molar absorbancy index of 17.6 $M^{-1} \text{ cm}^{-1}$ for $\text{Cr}(\text{enH})(\text{OH}_2)_5^{4+}$ at 510 $m\mu$ vs. $15.2 \pm 0.6 M^{-1} \text{ cm}^{-1}$ determined directly on chromatographically isolated $\text{Cr}(\text{enH})(\text{OH}_2)_5^{4+}$ in 3 *F* HClO_4 or in 0.1 *F* HClO_4 -0.05 *F* NaClO_4 at 20–25°, whereas the computer output values of the molar absorbancy indices of $\text{Cr}(\text{en})(\text{OH}_2)_4^{3+}$ and $\text{Cr}(\text{OH}_2)_6^{3+}$ at 510 $m\mu$ were within 5% of the experimental values. Hence, a "four-variable" program, identical with the "five-variable" program except for fixing the above molar absorbancy

TABLE I
FIRST-ORDER RATE CONSTANTS FOR AQUATION OF
Cr(enH)(OH₂)₅⁴⁺ IN AQUEOUS HClO₄ IN THE DARK

Temp, °C	[HClO ₄], F	C ₀ , mM	μ, M ^a	10 ³ k ₂ , sec ⁻¹
59.90	3.0	3.16	3.0	0.16 ± 0.04 ^{b,c}
59.90	3.0	3.16	3.0	0.22 ± 0.04 ^{b,c}
59.90	0.10	4.14	3.0	0.23 ± 0.02 ^{b,d}
59.90	0.031	3.30	3.0	0.11 ± 0.01 ^{b,c}
59.90	0.031	3.24	3.0	0.16 ± 0.06 ^{b,c}
59.90	0.10	5.03	0.5	0.22 ± 0.09 ^{b,c}
59.90	0.10	3.50	0.15	0.19 ± 0.02 ^{b,d}
59.90	0.10	3.42	0.15	0.23 ± 0.07 ^{d,e}
59.90	0.10	3.39	0.15	0.20 ± 0.02 ^{b,d}
80.02	3.0	5.35	3.0	1.49 ± 0.04 ^{d,e}
80.02	3.0	3.14	3.0	1.50 ± 0.08 ^{d,e}
80.02	3.0	3.09	3.0	1.49 ± 0.15 ^{b,d}
80.02	3.0	2.77	3.0	1.36 ± 0.11 ^{d,e}
80.02	3.0	2.70	3.0	1.45 ± 0.30 ^{b,d}
80.02	3.0	2.64	3.0	1.32 ± 0.11 ^{d,e}
80.02	3.0	2.55	3.0	1.25 ± 0.06 ^{d,e}
80.02	0.10	4.31	3.0	1.54 ± 0.11 ^{b,d}
80.02	0.10	4.31	3.0	1.62 ± 0.12 ^{d,e}
80.02	0.10	3.92	3.0	1.63 ± 0.36 ^{b,c}
80.02	0.031	3.21	3.0	1.60 ± 0.11 ^{b,d}
80.02	0.031	3.21	3.0	1.98 ± 0.50 ^{d,e}
80.02	0.10	3.97	0.50	1.58 ± 0.10 ^{b,d}
80.02	0.10	4.14	0.15	3.41 ± 0.89 ^{b,c}
84.91	3.0	6.47	3.0	2.16 ± 0.17 ^{d,e}
84.91	3.0	4.90	3.0	2.10 ± 0.05 ^{d,e}
84.91	3.0	4.08	3.0	2.18 ± 0.19 ^{b,d}
89.82	3.0	6.21	3.0	3.93 ± 0.24 ^{d,e}
89.82	3.0	4.00	3.0	4.14 ± 0.20 ^{b,d}
89.82	3.0	3.54	3.0	4.19 ± 0.31 ^{d,e}
89.82	3.0	3.52	3.0	4.35 ± 0.34 ^{b,c}
89.82	3.0	2.41	3.0	4.06 ± 0.14 ^{d,e}
89.82	0.10	4.72	3.0	4.03 ± 0.05 ^f
89.82	0.10	3.92	3.0	4.50 ± 0.41 ^{b,c}
89.82	0.095	5.25	2.9	4.07 ± 0.15 ^{d,e}
89.82	0.050	4.53	3.0	3.09 ± 0.63 ^{b,c}
89.82	0.031	3.15	3.0	4.67 ± 0.64 ^{b,c}
89.82	0.031	3.15	3.0	4.33 ± 0.21 ^f
89.82	0.10	3.97	0.50	5.52 ± 0.40 ^{b,d}
89.82	0.10	4.13	0.15	6.8 ± 1.5 ^{d,e}

^a Ionic strength, controlled with NaClO₄. ^b Five-variable computer program value, 510-mμ data. ^c Error based on per cent difference from the four-variable computer program value of *k*₂, relative to the five-variable computer program value—see text. ^d Estimated standard deviation; for computer values of *k*₂ the error referred to in footnote *c* is less than this estimated standard deviation. ^e Run started with chromatographically separated Cr(enH)(OH₂)₅⁴⁺; weighted average of data at 540 (or 550) and 385 (or 400) mμ, which nearly always agreed within the error given. ^f Same as footnote *e*, except 510-mμ data.

index at the 15.2 M⁻¹ cm⁻¹ experimental value, was run. This gave *k*₂ (and *k*₁ and *a*_M) values still in acceptable agreement with many of the "five-variable" program values of *k*₂ (and *k*₁ and *a*_M); in some runs per cent differences in *k*₂ were 15–60%. We have therefore based the errors of certain of the computer values of *k*₂ (designated in Table I with footnote *c*) on this percentage difference in *k*₂ between the "four-variable" and the "five-variable" program values. The errors given by this procedure are conservative and may well be the equivalent of 2 standard deviations, since the artificial restraint of a fixed parameter in the "four-variable" program probably leads to a

less accurate locating of the error minimum in the computer procedure.

Hydrolysis of Cr(en)(OH₂)₄³⁺.—Preliminary experiments indicated that the rates of the primary and secondary hydrolysis of Cr(en)(OH₂)₄³⁺ were not greatly different and that a consecutive first-order kinetics treatment would be necessary to evaluate *k*₁, which is defined by

$$-d(\text{Cr(en)(OH}_2)_4^{3+})/dt = k_1(\text{Cr(en)(OH}_2)_4^{3+}) \quad (4)$$

from spectrophotometric data.

Values of *k*₁, obtained by the "five-variable" computer program (see Experimental Section), are given in Table II. Error analysis was made in the same way as for *k*₂.

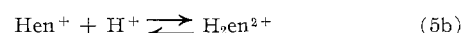
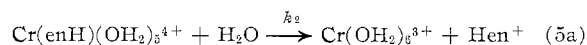
TABLE II
FIRST-ORDER RATE CONSTANTS FOR HYDROLYSIS OF
Cr(en)(OH₂)₄³⁺ IN AQUEOUS HClO₄ IN THE DARK

Temp, °C	[HClO ₄], F	C ₀ , mM	μ, M ^a	10 ³ k ₁ , sec ⁻¹
59.90	3.0	3.16	3.0	0.30 ± 0.03 ^{b,d}
59.90	3.0	3.16	3.0	0.30 ± 0.02 ^{b,d}
59.90	0.10	4.14	3.0	0.41 ± 0.03 ^{b,d}
59.90	0.031	3.30	3.0	0.42 ± 0.03 ^{b,d}
59.90	0.031	3.24	3.0	0.44 ± 0.03 ^{b,d}
59.90	0.10	5.03	0.50	0.58 ± 0.06 ^{b,d}
59.90	0.10	3.50	0.15	0.58 ± 0.13 ^{b,c}
59.90	0.10	3.39	0.15	0.55 ± 0.08 ^{b,c}
80.02	3.0	3.09	3.0	2.77 ± 0.25 ^{b,d}
80.02	3.0	2.70	3.0	3.28 ± 0.60 ^{b,d}
80.02	0.10	4.31	3.0	4.31 ± 0.85 ^{b,c}
80.02	0.10	3.92	3.0	4.32 ± 0.42 ^{b,d}
80.02	0.031	3.21	3.0	4.41 ± 0.76 ^{b,c}
80.02	0.10	3.97	0.50	6.0 ± 1.0 ^{b,c}
80.02	0.10	4.14	0.15	5.08 ± 0.50 ^{b,d}
84.91	3.0	4.08	3.0	4.86 ± 0.40 ^{b,d}
89.82	3.0	4.00	3.0	8.50 ± 0.80 ^{b,d}
89.82	3.0	3.52	3.0	8.35 ± 0.80 ^{b,d}
89.82	0.10	3.92	3.0	11.5 ± 1.2 ^{b,d}
89.82	0.050	4.53	3.0	12.9 ± 2.5 ^{b,c}
89.82	0.031	3.15	3.0	13.1 ± 2.4 ^{b,c}
89.82	0.10	4.13	0.50	14.8 ± 1.8 ^{b,c}

^{a-d} Footnotes are the same as in Table I.

Discussion

Figure 1 presents the visible absorption spectra of Cr(en)(OH₂)₄³⁺,¹⁸ Cr(enH)(OH₂)₅⁴⁺, and Cr(OH₂)₆³⁺ and shows that spectral scans from 700 to 360 mμ during aquation of Cr(enH)(OH₂)₅⁴⁺ to Cr(OH₂)₆³⁺ should give a single isosbestic point at 606 ± 2 mμ (*a*_M 9.9 ± 0.5 M⁻¹ cm⁻¹) and a region of near-tangency around 430 mμ (*a*_M 10 M⁻¹ cm⁻¹). Experimentally (see curves B of Figure 2 for a typical run) we find a well-defined isosbestic point at 603 ± 4 mμ (*a*_M 10.6 ± 1.0 M⁻¹ cm⁻¹) and the expected region of near-tangency over 2–3 half-lives, in good agreement with the theoretical values for the reaction



(18) The average maxima and minima found for chromatographed Cr(en)(OH₂)₄³⁺ in 0.1–3 F HClO₄ at 20–25° are 385 (max, *a*_M 24.3), 433 (min, *a*_M 10.7), 512 (max, *a*_M 41.7), 660 (min, *a*_M 0.5), and 666 mμ (max, 1.4 M⁻¹ cm⁻¹); these values are believed to be more accurate than those reported earlier by House and Garner.⁵

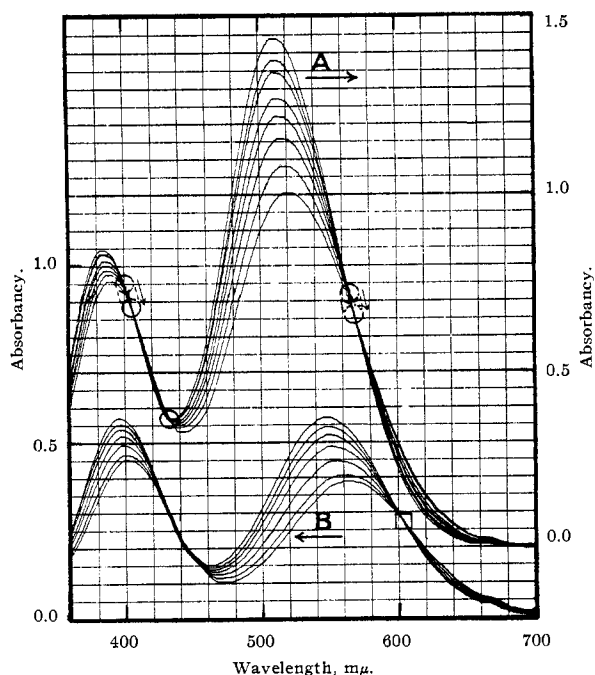


Figure 2.—Change in absorption spectra during hydrolysis: A, $\text{Cr(en)(OH}_2)_4^{3+}$ ($C_0 = 3.52 \text{ mM}$) in 3.0 F HClO_4 at 89.82° , reading downward at $500 \text{ m}\mu$, reaction time is 0, 15, 25, 45, 60, 80, 110, and 140 min, respectively; B, $\text{Cr(enH)(OH}_2)_5^{4+}$ ($C_0 = 2.64 \text{ mM}$) in 3.0 F HClO_4 at 80.02° , reading downward at $500 \text{ m}\mu$, reaction time is 0, 110, 230, 440, 800, 1340, and 1700 min, respectively. For curves A the positions of the initial isosbestic points are evident only for the first several scans and cannot be readily seen in the figure.

Weighted averages of $10^5 k_2$ from the 3 F HClO_4 data of Table I are 0.19 ± 0.03 , 1.42 ± 0.15 , 2.13 ± 0.09 , and $4.04 \pm 0.18 \text{ sec}^{-1}$ at 60, 80, 85, and 90° , respectively.¹⁹ At $\mu = 3 \text{ M}$, k_2 is essentially constant within experimental error over the range $0.03\text{--}3 \text{ F HClO}_4$, thus showing that the reaction is aquation, without appreciable contribution from base hydrolysis. Little or no effect of ionic strength on k_2 is observed in 0.1 F HClO_4 over the range $\mu = 0.15\text{--}3 \text{ M}$ at 60, 80, and 90° . An Arrhenius plot of the above values of $10^5 k_2$ in 3 F HClO_4 is slightly curved; from it we calculate $E_a = 25.4 \pm 2.3 \text{ kcal mole}^{-1}$, $\log PZ (\text{sec}^{-1}) = 10.9 \pm 1.5$, and $\Delta S^\ddagger_{333} = -11 \pm 7 \text{ cal deg}^{-1} \text{ mole}^{-1}$.

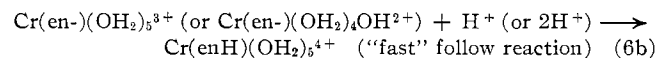
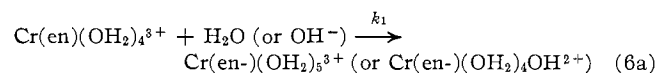
Schläfer and Kollrack² deduced a value of $0.22 \times 10^{-5} \text{ sec}^{-1}$ for k_2 (their k_3'') and $28 \text{ kcal mole}^{-1}$ for E_a in 0.1 F HClO_4 ($\mu = 0.15 \text{ M}$, NaClO_4) at 60° , their maximum run temperature. The weighted average of our k_2 values under these same conditions is $(0.21 \pm 0.02) \times 10^{-5} \text{ sec}^{-1}$, in excellent agreement with their value; our E_a is $25.4 \pm 2.3 \text{ kcal mole}^{-1}$ for these conditions. The agreement is partly fortuitous. It was possible for Schäfer and Kollrack to obtain approximate values of k_2 despite only a poor knowledge of the pentaquo intermediate spectrum²⁰ because most of the pre-

(19) The k_2 values from the runs made with chromatographically isolated $\text{Cr(enH)(OH}_2)_5^{4+}$ were weighted twice as heavily as computer k_2 values from the runs initiated with $\text{Cr(en)(OH}_2)_4^{3+}$; a small trend in k_2 with decreasing C_0 at 80° was ignored since it is not greatly beyond the experimental error, and since no trend was apparent at the other temperatures.

(20) They reported only a single point on their deduced spectrum of $\text{Cr(enH)(OH}_2)_5^{4+}$, namely, $a_M 20 \pm 11 \text{ M}^{-1} \text{ cm}^{-1}$ at $480 \text{ m}\mu$, at which wavelength we find $a_M 7.8 \pm 0.5 \text{ M}^{-1} \text{ cm}^{-1}$.

cursors of $\text{Cr(enH)(OH}_2)_5^{4+}$ in a *cis*- $\text{Cr(en)}_2(\text{OH}_2)_2^{3+}$ hydrolysis solution at late reaction times have been reduced to relatively low concentrations and the product $\text{Cr(OH}_2)_6^{3+}$ has a known absorption spectrum.

Figure 1 indicates that spectral scans from 700 to $360 \text{ m}\mu$ in sufficiently early stages of hydrolysis of $\text{Cr(en)(OH}_2)_4^{3+}$ to $\text{Cr(enH)(OH}_2)_5^{4+}$ should give three isosbestic points at 402 ± 2 ($a_M 21.3 \pm 1.0$), 434 ± 2 ($a_M 10.7 \pm 0.7$), and $566 \pm 2 \text{ m}\mu$ ($a_M 20.6 \pm 0.6 \text{ M}^{-1} \text{ cm}^{-1}$). At late reaction times, the two low-wavelength "isosbestic points" should become indistinct and progress into a state of near-tangent curves, and the high-wavelength "isosbestic point"²¹ should progress toward higher wavelength and lower absorbancy until, when essentially 100% of the $\text{Cr(en)(OH}_2)_4^{3+}$ has reacted to intermediate and hexaquo complexes, a final value of $606 \text{ m}\mu$ ($a_M 9.9 \text{ M}^{-1} \text{ cm}^{-1}$) is attained. Experimentally (see curve A of Figure 2 for a typical run up to *ca.* 1 half-life) this is the behavior found, the *initial* isosbestic points being within $\pm 2 \text{ m}\mu$ and $\pm 0.7 \text{ M}^{-1} \text{ cm}^{-1}$ of the predicted *initial* values for the reaction



and the high-wavelength "isosbestic point" showing the expected migration.

Weighted averages of $10^5 k_1$ from the 3 F HClO_4 data of Table II are 0.30 ± 0.02 , 2.92 ± 0.35 , 4.86 ± 0.40 , and $8.42 \pm 0.60 \text{ sec}^{-1}$ at 60, 80, 85, and 90° , respectively.

At 60, 80, and 90° and at $\mu = 3 \text{ M}$, plots of k_1 vs. $1/(\text{H}^+)$, where (H^+) is taken as the formal concentration of HClO_4 ($3\text{--}0.03 \text{ F}$), show an increase in k_1 with decreasing acidity. Despite the large errors and consequent uncertainty in shape of each curve, the plots are not linear and there appears to be a definite tendency for each curve to level out in the $0.1\text{--}0.03 \text{ F HClO}_4$ region. Base hydrolysis is probably unimportant at these acidities (analogy with related Cr(III) complexes supports such a conclusion) because, if it were involved, there would have to be some inhibiting effect of H^+ in the 3 F HClO_4 region, which seems unlikely. If hydroxoquo species were produced by proton removal in the 0.03 F HClO_4 region, they probably would be more labile, and, in order to account for the apparent nearly leveling off of k_1 , one would have to assume that they were less labile and predominate. Moreover, this explanation appears to be ruled out by the fact that the visible absorption spectra of $\text{Cr(en)(OH}_2)_4^{3+}$ and $\text{Cr(enH)(OH}_2)_5^{4+}$ are changed little in going from 3 to 0.03 F HClO_4 . No fully satisfying explanation has occurred to us. Worthy of mention is our finding that in $\text{Cr(en)(OH}_2)_4^{3+}$ solutions made basic with NaOH to pH 9–10 the $512\text{-m}\mu$ band shifts upscale to $563 \text{ m}\mu$

(21) By "isosbestic point" we mean here the successive intersections of successive pairs of spectral scans; because the concentration ratio of the products $\text{Cr(enH)(OH}_2)_5^{4+}$ and $\text{Cr(OH}_2)_6^{3+}$ is changing with time, there are no true (fixed) isosbestic points.

(little intensity change), but the 385-m μ band shifts downscale to 373 m μ and increases 15-fold in intensity in 5 min and still more in 10 min at 20–25°, after which reacidification to pH 0–1 with HClO₄ results in a spectrum with absorption bands at 517 and 361 m μ (intensities nearly equal). If the reacidification is made after only 3 min, the spectrum returns nearly to that of Cr(en)(OH₂)₄³⁺. Emerson and Graven¹² have reported a somewhat similar spectral change of Cr(OH₂)₆³⁺ on increase of pH from 2.3 to 4.6, which they ascribed to formation of Cr(OH₂)₅OH²⁺, but both bands moved to longer wavelength (as expected for the proposed conversion) and the intensity increase of the lower wavelength band was much less dramatic. Thus, at sufficiently high pH, Cr(en)(OH₂)₄³⁺ (or hydroxoquo derivatives produced) shows irreversible, or perhaps slowly reversible, spectral changes which presumably reflect polymerization; such changes probably have little relation to the complex acid dependence of k_1 in 3–0.03 *F* HClO₄.

In 0.1 *F* HClO₄ of ionic strength 0.15–3.0 *M*, plots of log k_1 vs. $\sqrt{\mu}/(1 + \sqrt{\mu})$ at 60, 80, and 90° are not linear; errors in k_1 values involved are large, but the plots suggest an increase of 30–40% in k_1 on decreasing ionic strength from 3 to 0.5 *M*, then (at 60 and 80°) a decrease in k_1 of smaller amount on decreasing ionic strength to 0.15 *M*. This behavior roughly parallels the dependence of k_1 on 1/(H⁺), and may imply a significant contribution from specific salt or ion-pairing effects. Hence, we refer to the reaction of Cr(en)(OH₂)₄³⁺ in these acid media as “hydrolysis,” without any implication that the reaction is all, or even mainly, aquation. We incline to the opinion it is largely aquation.

An Arrhenius plot of the above values of 10⁵ k_1 in 3 *F* HClO₄ at 60, 80, 85, and 90° is linear, giving $E_a = 27.7 \pm 1.5$ kcal mole⁻¹, log PZ (sec⁻¹) = 13.7 \pm 1.1, and $\Delta S^\ddagger_{333} = -3 \pm 5$ cal deg⁻¹ mole⁻¹. Within experimental error, Arrhenius plots at the other acidities and ionic strengths of Table II give the same E_a .

Schläfer and Kollrack² reported at their highest temperature, 60°, a value of 2.3×10^{-5} sec⁻¹

for k_1 (their k_3') and 31 kcal mole⁻¹ for E_a in 0.1 *F* HClO₄ ($\mu = 0.15$ *M*, NaClO₄), based on spectral change interpretations which led them to a kinetic treatment which assumed $k_1 \approx 10 k_2$. The weighted average of our k_1 values under these same conditions is $(0.56 \pm 0.10) \times 10^{-5}$ sec⁻¹, corresponding to $k_1/k_2 = 2.7 \pm 0.5$. The discrepancy appears to be due to errors in the Schläfer–Kollrack deduced spectra of Cr(en)(OH₂)₄³⁺ and Cr(enH)(OH₂)₅⁴⁺; an additional possible source of error is the fact that, at 25°, partial isomerization of *cis*-Cr(en)₂(OH₂)₂³⁺ to the *trans* form occurs with a rate comparable to that of the aquation of the former and was apparently not considered. We consider that Schläfer and Kollrack obtained remarkably good values of k_1 and k_2 considering the difficulties inherent in any attempted interpretation of the spectral changes occurring during conversion of *cis*-Cr(en)₂(OH₂)₂³⁺ to Cr(OH₂)₆³⁺ without benefit of direct knowledge of the spectra of any of the intermediates.

An alternative explanation of the Schläfer–Kollrack results is that the species they referred to as Cr(en)(OH₂)₄³⁺ is actually Cr(en)(enH)(OH₂)₃⁴⁺, which we would think may well hydrolyze with the rate they ascribe to the tetraquo complex (their k_3'). Their k_3'' may then be an unresolved rate constant for the kinetically overlapping primary and secondary hydrolysis of Cr(en)(OH₂)₄³⁺. We plan to attempt isolation of the above postulated intermediate, although the presence of isomers probably will complicate the isolation.

The fact that k_1 and k_2 are nearly equal under the conditions studied implies that the systems studied by Ohta, Matsukawa, and Tsuchiya³ were not at equilibrium, and that their “equilibrium constants” are not accurate.

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