

Conclusions

The esr investigations of the autoxidation of titanium(III) and vanadium(III) trisacetylacetonates in dilute single crystals of aluminum(III) trisacetylacetonate show that both of these complexes react by an attack of an oxygen molecule on the metal. The vanadium(III) is immediately converted to the vanadyl(IV) ion with the second oxygen atom presumably going off as O^+ to attack one of the rings. The titanium(III), however, appears to form a stable TiO_2^{3+}

peroxy radical. This radical, in solution or pure solid, is then able to attack another chelate molecule forming a dimeric species containing titanium-oxygen bridges.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE CATHOLIC UNIVERSITY OF AMERICA, WASHINGTON, D. C. 20017

Stoichiometry and Kinetics of the Acid Cleavage of Some Single-Bridged Binuclear Chromium(III) Complexes¹

BY DONALD W. HOPPENJANS AND JOHN B. HUNT

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The stoichiometry and kinetics of the cleavage of the rhodo ion, $(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$, the aquoerythro ion, $(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2^{5+}$, and the chloroerythro ion, $(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+}$, by aqueous $HClO_4$ have been studied. The products of the cleavage reactions are $(NH_3)_5CrOH_2^{3+}$ from the rhodo ion, $(NH_3)_5CrOH_2^{3+}$ and *cis*- $(NH_3)_4Cr(OH_2)_2^{3+}$ from the aquoerythro ion, and $(NH_3)_5CrOH_2^{3+}$ and *trans*- $(NH_3)_4Cr(OH)_2Cl^{2+}$ from the chloroerythro ion. The cleavage rates are independent of $[H^+]$ in 0.1–1.0 *M* $HClO_4$, the rate law being $-d[\text{dimer}]/dt = k[\text{dimer}]$, where $k = (7.6 \pm 0.1) \times 10^{-4} \text{ sec}^{-1}$ at 55.0° and $E_a = 28.7 \pm 0.3 \text{ kcal mol}^{-1}$ for the rhodo ion; $k = (11.8 \pm 0.4) \times 10^{-4} \text{ sec}^{-1}$ at 55.0° and $E_a = 28.1 \pm 0.3 \text{ kcal mol}^{-1}$ for the chloroerythro ion; $k = (4.0 \pm 0.3) \times 10^{-4} \text{ sec}^{-1}$ at 65.0° and $E_a = 28.7 \pm 0.4 \text{ kcal mol}^{-1}$ for the aquoerythro ion, all at $\mu = 1.00 \text{ M}$. The cleavage of the aquoerythro ion becomes more rapid in the presence of Cl^- , and *cis*- $(NH_3)_4Cr(OH_2)Cl^{2+}$ is found among the products. It is postulated that the aquoerythro ion reacts with Cl^- to give the *cis*-chloroerythro ion, which cleaves more rapidly than the aquoerythro ion.

Introduction

By now it is well established that the binuclear chromium(III) complexes of the rhodo-erythro series have as a common structural feature a single oxygen bridge.^{2–4} The present paper is concerned with the solution chemistry of three of these ions, the rhodo ion, $(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$, the aquoerythro ion, $(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2^{5+}$, and the chloroerythro ion, $(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+}$. These ions are all known to undergo cleavage to monomeric species in acidic solutions,^{2,3} the cleavage of the rhodo ion by hydrochloric acid being in fact the most convenient source of $[(NH_3)_5CrCl]Cl_2$.⁵ However, no quantitative data on the rates of acid cleavage have been published, and even the immediate products of acid cleavage are in doubt, since the reported products could in some cases have arisen by anation of the immediate cleavage products.^{2,3}

A more thorough investigation of the cleavage reactions of these ions seemed warranted for several reasons. These ions are among the few well-characterized binuclear complexes having a single hydroxo bridge, and they are probably similar to the intermediates involved in the acid cleavage of binuclear complexes with two hydroxo bridges.^{6,7} Since the ions of the erythro series contain a tetraammine fragment, they are potential sources of tetraamminechromium(III) complexes, some of which have not been synthesized heretofore. Further, the acid cleavage of these complexes represents an unusual sort of substitution reaction in that the leaving group bears a net positive charge; *e.g.*, in the cleavage of the rhodo ion the leaving group is $(NH_3)_5CrOH^{2+}$.

The aquoerythro and chloroerythro ions are capable of existing in two isomeric forms, *i.e.*, forms having the aquo or chloro ligand either *cis* or *trans* to the hydroxo bridge. Schwarzenbach and Magyar^{4,8} believed that the aquoerythro ion, formed by base hydrolysis of the

(1) Based on the Ph.D. Dissertation of D. W. Hoppenjans, May 1968. Supported by National Science Foundation Grant GP-5425.

(2) W. K. Wilmarth, H. Graf, and S. T. Gustin, *J. Am. Chem. Soc.*, **78**, 2683 (1956).

(3) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **299**, 15 (1959).

(4) G. Schwarzenbach and B. Magyar, *Helv. Chim. Acta*, **46**, 1425 (1962).

(5) G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., New York, N. Y., 1962, p 202.

(6) D. M. Grant and R. E. Hamm, *J. Am. Chem. Soc.*, **80**, 4166 (1958).

(7) R. E. Connick and M. G. Thompson, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, No. O-23 and O-24.

(8) G. Schwarzenbach and B. Magyar, *Helv. Chim. Acta*, **46**, 1454 (1962).

rhodo ion followed by the addition of acid, has the *trans* configuration. We will present evidence that the aquoerythro ion has the *cis* configuration and that the chloroerythro ion has the *trans* configuration. This report will deal also with the question of which of the two bonds between the chromium atoms and the bridging oxygen atoms is broken in the cleavage of the unsymmetrical dimers.

Experimental Section

Materials and Preparations.—Rhodo chloride, $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5]\text{Cl}_6$, was prepared and purified according to the method of Linhard and Weigel.³ The red compound contained varying amounts of water of crystallization, depending on the conditions of precipitation and drying, so that the ratio N/Cr was taken as the measure of the quality of the preparation. *Anal.* Calcd for $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5]\text{Cl}_6$: mole ratio N/Cr = 5.00. Found: mole ratio N/Cr = 5.10.

Aquoerythro chloride was prepared from rhodo chloride according to the method of Linhard and Weigel.³ *Anal.* Calcd for $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4\text{OH}_2]\text{Cl}_5 \cdot n\text{H}_2\text{O}$: mole ratio N/Cr = 4.50. Found: mole ratio N/Cr = 4.50.

Hydroxyerythro perchlorate, $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4\text{OH}](\text{ClO}_4)_4$, was prepared as follows. Aquoerythro chloride (10 g) was dissolved in 100 ml of H_2O and 10 ml of 2 *M* NH_3 was added. Saturated NaClO_4 (50 ml) was added, and the solution was allowed to stand in an ice bath for *ca.* 1 hr. The purple product was collected on a filter and washed with alcohol and ether. The NaClO_4 used in the recrystallization was prepared from Na_2CO_3 and HClO_4 to ensure freedom from Cl^- . The crude hydroxyerythro perchlorate (10 g) was dissolved in 50 ml of H_2O , 5 ml of 2 *M* NH_3 was added, and the chloride-free hydroxyerythro perchlorate was precipitated by the dropwise addition of 10 ml of saturated NaClO_4 solution to the ice-cold solution of the complex. The product was washed with alcohol and ether and air dried. The solution resulting from dissolving a sample of hydroxyerythro perchlorate in 1 *M* HClO_4 had a spectrum identical with that of a freshly prepared solution of aquoerythro chloride.

Chloroerythro chloride was prepared according to the method of Linhard and Weigel,³ *i.e.*, by heating aquoerythro chloride at 90° for several hours until the color had changed from bright red to violet. To convert the chloride salt to the perchlorate, 10 g of the chloride was mixed with 75 ml of 0.01 *M* HClO_4 , and 17 g of solid AgClO_4 was added slowly with vigorous stirring, the amounts chosen being such as to provide an excess of ionic Cl^- and prevent the loss of coordinated Cl^- . The solution was filtered to remove the AgCl which had formed. The filtrate was cooled in ice, 30 ml of 70% HClO_4 was added, the solution was again cooled in ice, and the precipitate of chloroerythro perchlorate was collected on a sintered-glass filter. The crude perchlorate was dissolved in 100 ml of 0.001 *M* HClO_4 , the solution was filtered to remove any residual AgCl , the filtrate was cooled in ice, and the chloroerythro perchlorate was precipitated by the dropwise addition of 30 ml of 70% HClO_4 . *Anal.* Calcd for $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4\text{Cl}](\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$: N, 16.55; Cr, 13.65; bound Cl, 4.67. Found: N, 16.39; Cr, 13.51; bound Cl, 4.65.

Solutions of aquoerythro perchlorate and rhodo perchlorate were prepared by dissolving the respective chloride salts in a very slight excess of a solution of AgClO_4 in *ca.* 0.001 *M* HClO_4 and filtering to remove the precipitate of AgCl .

The salt $[(\text{NH}_3)_5\text{CrOH}_2](\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$ was prepared by cleavage of the rhodo ion with 70% HClO_4 . Rhodo chloride (20 g) was ground to a fine powder and added with stirring to 100 ml of 70% HClO_4 . After the initially vigorous evolution of HCl had subsided, the mixture was heated at 70° for 2 hr while being stirred on a combination hot plate-magnetic stirrer. The suspension, which was now red-orange, was allowed to cool, and 300 ml of H_2O was added to aid in the transfer to the filter. The crude orange $[(\text{NH}_3)_5\text{CrOH}_2](\text{ClO}_4)_3$ was collected on a sintered-glass filter and purified by reprecipitation from very dilute HClO_4

by the addition of 70% HClO_4 . This method gives higher yields and is simpler than methods described previously.⁹ *Anal.* Calcd for $[(\text{NH}_3)_5\text{CrOH}_2](\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$: mole ratio N/Cr = 5.00. Found: mole ratio N/Cr = 5.07.

Caution! Although we have experienced no difficulties with the perchlorate salts of the complexes mentioned herein, these compounds should be treated as potentially explosive and handled with care.

$[(\text{NH}_3)_4\text{CrC}_2\text{O}_4]\text{ClO}_4$ was prepared by a method resembling the preparation of $[(\text{NH}_3)_4\text{CrC}_2\text{O}_4]\text{NO}_3$ described by Schlessinger.¹⁰ $[(\text{NH}_3)_5\text{CrOH}_2](\text{ClO}_4)_3$ (30 g) was added to 15 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ dissolved in 150 ml of a 1:1 ethanol-water solution. The mixture was heated at 60° and stirred vigorously until all of the aquopentaammine salt had dissolved (*ca.* 10 min). The solution was filtered while hot to remove the crystals of $[(\text{NH}_3)_4\text{CrC}_2\text{O}_4]\text{ClO}_4$ which had formed. The filtrate was heated for another 10 min at 60°, and another crop of crystals was collected from the hot solution. The crystals were washed with successive 50-ml portions of 1 *M* HClO_4 until the filtrate had changed from orange to almost colorless. The reaction mixture was cooled and treated with 70% HClO_4 to recover unreacted $[(\text{NH}_3)_5\text{CrOH}_2](\text{ClO}_4)_3$; yield, 15 g of $[(\text{NH}_3)_4\text{CrC}_2\text{O}_4]\text{ClO}_4$ and 8 g of $[(\text{NH}_3)_5\text{CrOH}_2](\text{ClO}_4)_3$ recovered from filtrate.

cis- $[(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}]\text{Cl}_2$ was prepared by the reaction of $[(\text{NH}_3)_4\text{CrC}_2\text{O}_4]\text{ClO}_4$ with 12 *M* HCl , as described by Schlessinger.¹¹ The raw product was dissolved in 1 *M* HClO_4 , filtered to remove any impurities of $[(\text{NH}_3)_5\text{CrOH}_2](\text{ClO}_4)_3$ or $[(\text{NH}_3)_5\text{CrCl}](\text{ClO}_4)_2$, and reprecipitated by the dropwise addition of 12 *M* HCl . The chloride was converted to the perchlorate by grinding it with cold 70% HClO_4 to expel the ionic Cl^- as HCl , adding sufficient water to dissolve the salt, and precipitating the perchlorate from ice-cold solution by the addition of 70% HClO_4 . The perchlorate salt was collected on a filter, washed with alcohol and ether, and air dried. *Anal.* Calcd for *cis*- $[(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}](\text{ClO}_4)_2$: N, 15.04; Cr, 13.96; Cl (excluding ClO_4^-), 9.51. Found: N, 14.90; Cr, 13.79; Cl (excluding ClO_4^-), 9.84.

To prepare *cis*- $[(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2](\text{ClO}_4)_3$, Cl^- was removed from *cis*- $[(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}]\text{Cl}_2$ by base hydrolysis. *cis*- $[(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}]\text{Cl}_2$ (10 g) was stirred into 50 ml of 1 *M* NaOH at *ca.* 25°, and stirring was continued for 5 min. The mixture was poured into 100 ml of ice-cold 70% HClO_4 , and the *cis*- $[(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2](\text{ClO}_4)_3$ which precipitated was collected on a suction filter. The first filtrate was used to transfer the remaining solid from the reaction flask to the filter. The product was washed generously with absolute ethanol and then with ether; yield, >95%. The salt was purified by recrystallization from the minimum volume of distilled water with 70% HClO_4 . *Anal.* Calcd for *cis*- $[(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2](\text{ClO}_4)_3$: N, 12.33; Cr, 11.44. Found: N, 12.61; Cr, 11.48.

To prepare *trans*- $[(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}]\text{Cl}_2$, 40 g of chloroerythro chloride was ground to a fine powder in a mortar, and 125 ml of 70% HClO_4 was added slowly with stirring, so as to permit the expulsion of most of the ionic chloride as HCl . When the evolution of HCl was essentially complete, the mixture was transferred to a flask and diluted to *ca.* 700 ml with distilled water. The mixture was heated at 60° with constant stirring until dissolution of the solid was nearly complete (20–30 min). The solution was filtered while hot and then cooled in ice. About 150 ml of 70% HClO_4 was added, and the precipitate of $[(\text{NH}_3)_5\text{Cr}(\text{OH}_2)](\text{ClO}_4)_3$ (25–30 g) was removed by filtration. *trans*- $[(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}]\text{Cl}_2$ precipitated from the ice-cold filtrate upon the addition of 400 ml of 12 *M* HCl . The small brownish crystals were collected on a filter and washed with alcohol and ether. The salt was recrystallized by dissolving it in the minimum amount of 0.01 *M* HCl and adding an equal volume of 12 *M* HCl to the ice-cold solution dropwise with stirring; yield, 15 g. *Anal.* Calcd for *trans*- $[(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}]\text{Cl}_2$: N, 22.91; Cr, 21.27.

(9) See ref 5, p 198.

(10) See ref 5, p 225.

(11) See ref 5, p 226.

Found: N, 22.76; Cr, 20.84; bound Cl, 1.00 ± 0.01 mol/mol of Cr.

To prepare *trans*-[(NH₃)₄Cr(OH₂)Cl](ClO₄)₂, the chloride salt (50 g) was ground to a fine powder in a mortar and 100 ml of 70% HClO₄ was added slowly with stirring to expel the ionic chloride as HCl. The crude perchlorate was collected on a sintered-glass filter, the first portion of the filtrate being used to aid the transfer of the solid. The crude product was dissolved in the minimum amount of water and recrystallized by the addition of two volumes of 70% HClO₄; yield, 60 g. Further purification was effected by recrystallization from methanol, in which the major impurities, [(NH₃)₅CrCl](ClO₄)₂ and [(NH₃)₅Cr(OH₂)](ClO₄)₃, are insoluble and *trans*-[(NH₃)₄Cr(OH₂)Cl](ClO₄)₂ is abundantly soluble. *Anal.* Calcd for *trans*-[(NH₃)₄Cr(OH₂)Cl](ClO₄)₂·nH₂O: mole ratio N/bound Cl/Cr = 4.00/1.00/1. Found: mole ratio N/bound Cl/Cr = 3.98/1.02/1.

trans-[(NH₃)₄Cr(OH₂)₂](ClO₄)₃ was prepared from *trans*-[(NH₃)₄Cr(OH₂)Cl]Cl₂ by a procedure exactly analogous to that described above for the preparation of *cis*-[(NH₃)₄Cr(OH₂)₂](ClO₄)₃; yield, 16 g from 10 g of the chloroquo chloride. *Anal.* Calcd for *trans*-[(NH₃)₄Cr(OH₂)₂](ClO₄)₃: N, 12.33; Cr, 11.44. Found: N, 12.40; Cr, 11.52.

Sodium perchlorate solutions for kinetics experiments were prepared by the careful neutralization of NaOH with HClO₄. All other chemicals were J. T. Baker reagent grade.

Analytical Procedures.—The boric acid modification¹² of the Kjeldahl method was used for nitrogen analyses. A sample of the complex to be analyzed was digested with NaOH, and the NH₃ which was released was distilled into a saturated solution of boric acid. The ammonium borate which was formed was titrated with HClO₄ solution previously standardized against NH₃ released from NH₄Cl by the same digestion procedure. Samples to be analyzed for chromium were oxidized to CrO₄²⁻ with alkaline peroxide, and the CrO₄²⁻ was determined either spectrophotometrically¹³ from the absorbance at 373 mμ or volumetrically¹⁴ by titration of the acidified solution with a standard Fe²⁺ solution. Samples to be analyzed for chloride were digested with base, acidified, and then titrated against standard AgNO₃ solution to a potentiometric end point.

Spectra.—Absorption spectra were recorded using a Cary Model 15 spectrophotometer. In the determination of extinction coefficients of solid complexes, three samples were weighed out simultaneously. One of these was dissolved in a known volume of solution (usually 1 M HClO₄) and its spectrum was recorded. The remaining samples were analyzed for chromium volumetrically,¹⁴ so that the extinction coefficients reported were calculated from the absorbance and the concentration of chromium as determined by analysis.

Ion-Exchange Separations.—As an aid in establishing reaction stoichiometry, the complexes present in solution at various stages of reaction were separated by chromatography on cation-exchange columns. The conditions for elution of the various species were established using solutions of pure complex salts and synthetic mixtures of these. To separate complexes of the same charge, long columns (*ca.* 40 cm) of Dowex 50W-X2 resin, H⁺ form (generally 100–200 mesh), were used. To separate complexes of different charges, Dowex 50W-X8 resin, H⁺ form, was used. In a typical experiment a weighed sample of the dimer salt was dissolved in the reaction medium at the temperature of the run and diluted to the mark in a volumetric flask. The flask was suspended in a thermostated bath, and aliquots were withdrawn periodically, quenched by cooling, and placed on the ion-exchange columns. Separation and elution of the various complexes was accomplished with perchloric acid solutions. In cases of complexes of high charge which adhered strongly to the resin, the columns were cut after the complexes had separated into

bands, and the complex present in each section was removed batchwise with *ca.* 5 M HClO₄. The complex present in each portion of the effluent was identified by its spectrum, and the chromium content was determined by analysis. In this way the concentration of each complex present in solution at the time of sampling could be determined with a precision of 10% or better.

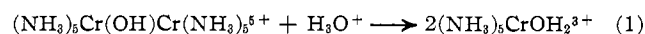
Kinetic Runs.—For the most part the progress of the acid-cleavage reactions was followed spectrophotometrically by recording the change in absorbance at fixed wavelengths as a function of time. To begin a run, either a weighed sample of the perchlorate salt or an aliquot of a solution of the perchlorate salt was added to a volumetric flask containing an NaClO₄–HClO₄ solution at the temperature of the run. The solution was diluted to the mark and mixed thoroughly, and a sample was transferred to a cell contained in the thermostated ($\pm 0.05^\circ$) cell compartment of the Cary Model 15 spectrophotometer. In the early runs the temperature in the cell was monitored by means of a thermistor fitted through the lid of the cell and immersed in the solution. In later runs the cell was immersed in a water bath built into the cell compartment, and the temperature within the cell was taken to be that of the bath.

In some runs the progress of the reaction was followed by measuring the rate of consumption of acid at a fixed pH, using a Sargent recording pH Stat. Prior to each such run the pH Stat was calibrated at pH 7 and 2, using standard buffers at the temperature of the run. The titrant used in these runs was a standard solution *ca.* 0.1 M in HClO₄ and 0.9 M in NaClO₄. The reaction medium was 1.00 M NaClO₄, adjusted to the temperature and pH of the run by means of the instrument. The run was initiated by dissolving a weighed sample of the dimer salt in the reaction medium.

Evaluation of Kinetic Data.—In those cases in which a steady absorbance was achieved at long reaction times, first-order rate constants, *k*, were obtained from the slopes of plots of $\log (A_t - A_\infty)$ vs. time, using the equation $kt = \ln [(A_0 - A_\infty)/(A_t - A_\infty)]$, where *A*₀, *A*_∞, and *A*_{*t*} are the absorbance at time zero, infinite time, and *t*, respectively. Where a steady absorbance was not achieved at long reaction times, rate constants were obtained by the method of Guggenheim,¹⁵ either graphically from the slopes of plots of $\ln (A_t - A_{t+\tau})$ vs. time or by means of a nonlinear least-squares computer program. First-order rate constants were obtained from the pH Stat data from plots of $\log (V_\infty - V_t)$, using the equation $kt = \ln [V_\infty/(V_\infty - V_t)]$, where *V*_∞ and *V*_{*t*} are the volumes of titrant that had been delivered at infinite time and at time *t*, respectively, in order to maintain a constant pH.

Results

Cleavage of the Rhodo Ion.—When the rhodo ion reacted in 0.1–1.0 M HClO₄ until a steady absorbance was achieved, the spectrum of the product solution was indistinguishable from that of a solution of [(NH₃)₅CrOH₂](ClO₄)₃. When reacted solutions were run through cation-exchange columns, only one product band was observed, and [(NH₃)₅CrOH₂](ClO₄)₃ could be precipitated from the column effluent.¹⁶ The stoichiometry of the cleavage reaction is then



as reported earlier by Linhard and Weigel.³

First-order rate constants for the cleavage reaction of the rhodo ion are given in Table I. The rate plots from which these rate constants were derived were linear for at least 3 half-lives, confirming both the

(12) A. I. Vogel, "Quantitative Inorganic Analysis," John Wiley & Sons, Inc., New York, N. Y., 1961, p 257.

(13) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

(14) See ref 12, pp 286, 311, 953.

(15) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

(16) These results are further evidence that (NH₃)₅CrOH₂³⁺ is more robust in ClO₄⁻ solutions than in NO₃⁻ solutions. See N. V. Duffy and J. E. Early, *J. Am. Chem. Soc.*, **89**, 272 (1967).

first-order kinetics and good stoichiometry of the reaction. The rate constants are independent of hydrogen ion concentration over the range studied, the experimental rate law being

$$-d[\text{dimer}]/dt = k[\text{dimer}] \quad (2)$$

TABLE I
FIRST-ORDER RATE CONSTANTS FOR THE CLEAVAGE OF
(NH₃)₅Cr(OH)Cr(NH₃)₅⁵⁺ IN HClO₄ SOLUTIONS^a

[H ⁺], M	10 ⁴ k, sec ⁻¹		
	45.0°	50.0°	55.0°
1.0	2.01 (3)	4.04 (3)	7.54 (2)
0.8	2.02 (2)	3.94 (3)	7.74 (2)
0.6		3.89 (2)	7.61 (2)
0.4	1.99 (4)		
0.2	1.94 (1)	3.86 (1)	7.50 (3)
0.1		3.87 (1)	7.50 (1)

^a Measured spectrophotometrically at 500 mμ. μ = 1.00, adjusted with NaClO₄. Numbers in parentheses show the number of measurements.

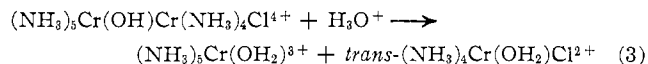
Cleavage of the Chloroerythro Ion.—When solutions of chloroerythro perchlorate in 1 M HClO₄ were heated at 50°, a change in the spectrum was observed which was substantially complete after 1.5 hr. Titration of free chloride at various stages of the reaction showed that only a small fraction of the bound chloride ion was released during the time required for near completion of the spectral change, implying that the cleavage reaction of the dimer was considerably more rapid than the replacement of chloride either from the dimer or from its cleavage products. This implication was confirmed by several lines of evidence. When partially reacted solutions were placed on cation-exchange columns, two major product bands were observed. The band which eluted most readily (with 1 M HClO₄ from Dowex 50W-X8) had a Cl/Cr mole ratio of 1/1, and its spectrum was in quantitative agreement with that of very pure *trans*-(NH₃)₄Cr(OH₂)Cl²⁺. The second band, which eluted from Dowex 50W-X2 resin with 2.5 M HClO₄, had absorption maxima at 362 and 478 mμ and a minimum at 415 mμ, as does (NH₃)₅CrOH₂³⁺, and the extinction coefficients were similar to, though not in quantitative agreement with, those of (NH₃)₅CrOH₂³⁺.¹⁷

The addition of 70% HClO₄ caused precipitation of [(NH₃)₅Cr(OH₂)](ClO₄)₃ from the effluent containing the second band. That the reaction responsible for the spectral change is cleavage, rather than replacement of chloride ion, is indicated also by the good agreement between the rate constants determined spectrophotometrically and those obtained by following the consumption of hydrogen ion (see Table II). This

(17) In every experiment the quantity of chromium in the second band exceeded that in the first. The extinction coefficients of the second band were slightly higher at 362 mμ and slightly lower at 478 mμ than those of (NH₃)₅CrOH₂³⁺, and the minimum at 415 mμ was not as deep as for pure (NH₃)₅CrOH₂³⁺, as would be expected if some *trans*-(NH₃)₄Cr(OH₂)Cl²⁺, from the aquation of *trans*-(NH₃)₄Cr(OH₂)Cl²⁺, were present. Also, cleavage of the dimer on the column, which does occur and is more rapid at high ionic strengths, would tend to make the chromium content of the second band higher than that of the first. Aquation of *trans*-(NH₃)₄Cr(OH₂)Cl²⁺ would have the same effect.

conclusion is supported also by the high yields of (NH₃)₄Cr(OH₂)Cl²⁺ obtained in the reaction of the chloroerythro ion with perchloric acid (see Experimental Section).

The stoichiometry of the cleavage reaction of the chloroerythro ion is expressed by eq 3. As expected



from eq 3, the consumption of 1 mol of hydrogen ion per mole of dimer was observed in the pH Stat runs.

Plots of log (A_t - A_∞) vs. time were linear for at least 3 half-lives, as were plots of log (V_∞ - V_t) vs. time for the pH Stat runs at pH 2. Runs at pH >2 gave curved plots, and the color changes were not those observed at higher acidities.

First-order rate constants for the cleavage reaction of the chloroerythro ion are recorded in Table II. It is seen that the rate of cleavage is independent of hydrogen ion concentration over the range studied, so that the experimental rate law for this dimer as well has the form of eq 2.

TABLE II
FIRST-ORDER RATE CONSTANTS FOR THE CLEAVAGE OF
(NH₃)₅Cr(OH)Cr(NH₃)₄Cl⁴⁺ IN PERCHLORIC ACID SOLUTIONS^a

[H ⁺], M	10 ⁴ k, sec ⁻¹				
	40.0°	45.0°	50.0°	55.0°	60.0°
1.0	1.42 (3)	...	5.8 (5)	11.9 (6)	22.1 (2)
0.5	5.9 (1)	12.2 (2)	22.1 (1)
0.2	10.9 (2)	...
0.01	1.48 (2) ^b	3.04 (3) ^b

^a Ionic strength = 1.0, adjusted with NaClO₄. Numbers in parentheses show the number of measurements. Rate constants measured spectrophotometrically at 500 mμ, unless otherwise noted. ^b From pH Stat runs.

Cleavage of the Aquoerythro Ion.—The reaction of the aquoerythro ion with perchloric acid solutions was found to be much slower than the reactions of the rhodo and chloroerythro ions. At 65° a period of about 3 hr was required for substantial completion of the reaction, as indicated by changes in the absorption spectrum, and a steady absorbance was never achieved, even at very long reaction times. In Figure 1 the

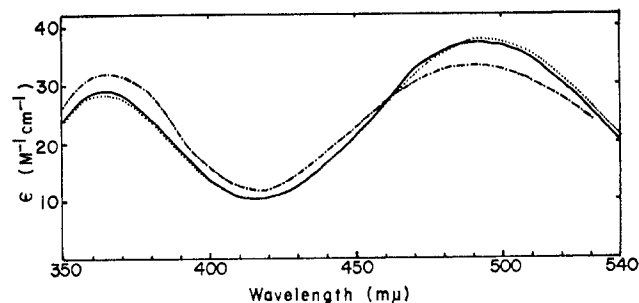


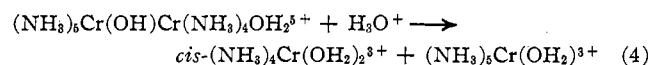
Figure 1.—Observed spectrum (solid line) of solution of aquoerythro ion in 1 M HClO₄ which had reacted for 64 min at 70° compared with the spectrum calculated assuming the products to be a 1:1 mixture of (NH₃)₅CrOH₂³⁺ and *cis*-(NH₃)₄Cr(OH₂)₂³⁺ (.....) and with the spectrum calculated assuming the products to be a 1:1 mixture of (NH₃)₅CrOH₂³⁺ and *trans*-(NH₃)₄Cr(OH₂)₂³⁺ (-----).

spectrum of a solution of aquoerythro perchlorate which had reacted for about 2 half-times is compared to spectra calculated for mixtures of unreacted aquoerythro ion with two possible combinations of products, $(\text{NH}_3)_5\text{Cr}(\text{OH})_2^{3+}$ and *cis*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$ or $(\text{NH}_3)_5\text{Cr}(\text{OH}_2)_2^{3+}$ and *trans*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$. It is seen that the observed spectrum agrees very well with that calculated assuming *cis*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$ to be the tetraammine product. However, it is seen that the observed spectrum does not differ widely from that calculated assuming the tetraammine product to be *trans*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$. Figure 1 is consistent with the conclusion that the major tetraammine product is the *cis* isomer, but the formation of a substantial proportion of the *trans* isomer cannot be ruled out on the basis of Figure 1.

Isosbestic points proved to be of little use in deciding whether cleavage of the aquoerythro ion gave *cis*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$, *trans*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$, or a mixture of the two isomers. The spectra of the aquoerythro ion and the mixture of its reaction products cross at *ca.* 437, 463, and 355 $m\mu$, but the isosbestic points are not at all sharp because the spectra are rising sharply and are nearly parallel in these regions. Further, it is obvious from Figure 1 that only a small difference in isosbestic points would result if *trans*- rather than *cis*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$ were the tetraammine product.

More conclusive evidence concerning reaction stoichiometry was obtained from ion-exchange separation of products. Only a partial separation of products on Dowex 50W-X2 resin was achieved, since all of the possible products bear charge +3. However, the chromium concentration in the effluent from the cation-exchange columns went through maxima corresponding to elution of the various monomers (with 1 *M* HClO_4). Two such maxima were observed for solutions which had reacted for *ca.* 2 half-lives. The spectrum at the first maximum was that of *cis*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$ and the spectrum at the second maximum was that of $(\text{NH}_3)_5\text{Cr}(\text{OH}_2)_2^{3+}$. Solutions which had reacted for about 6 half-times contained an additional monomeric species. The spectrum at the first maximum for these solutions had absorption peaks at 508 and 380 $m\mu$, the respective absorbancies at these two peaks being in the ratio of about 1.25:1, which is similar to the spectrum of $(\text{NH}_3)_3\text{Cr}(\text{OH}_2)_3^{2+}$ reported by Schäffer and Anderson.¹⁸ No evidence was observed for *trans*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$ among the products for solutions which had reacted for short or long periods of time. Since the spectrum of *trans*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$ was found to change only slightly during 3 hr at 65° and since *trans*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{2+}$ could be separated by ion-exchange chromatography from synthetic mixtures with $(\text{NH}_3)_5\text{Cr}(\text{OH}_2)_2^{3+}$ and *cis*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$, we conclude from these observations that no appreciable quantity of *trans*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$ is formed in the cleavage of

the aquoerythro ion, since *trans*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$ would neither isomerize nor aquate appreciably during the time of the cleavage reaction. We conclude further that the stoichiometry of the cleavage reaction is described fairly well by the equation



Attempts to verify the stoichiometry of eq 4 by following the consumption of acid at pH 2 were unsuccessful. Rapid loss of NH_3 from the dimer was observed, possibly because an appreciable fraction of the dimer is in the form of its conjugate base at pH 2.⁴

The loss of NH_3 from the products would account for the continuing slow change in spectra of solutions at long reaction times and for the observation of the triaquo complex at long reaction times.

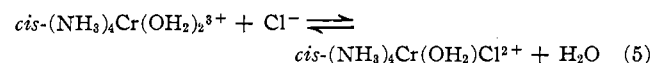
First-order rate constants for the cleavage of the aquoerythro ion in HClO_4 solutions are given in Table III. These rate constants were evaluated by the Guggenheim method, because of the decomposition of the products. It is seen from Table III that the reaction rate is independent of hydrogen ion concentration over the range 0.1–1 *M* HClO_4 , so that this reaction also obeys the rate law of eq 2.

TABLE III
FIRST-ORDER RATE CONSTANTS FOR THE CLEAVAGE OF
 $(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4\text{OH}_2^{5+}$ IN HClO_4 SOLUTIONS^a

[H ⁺], <i>M</i>	$10^4 k$, sec ⁻¹			
	60.0°	65.0°	70.0° ^b	75.0° ^b
1.0	2.3 (3)	3.8 (2), ^b 3.8 (1)	7.2 (2), 7.0 (2) ^c	13.0 (2)
0.8	...	4.0 (4)
0.6	2.3 (3)	4.1 (6)
0.4	2.7 (1)	4.0 (3)
0.2	2.5 (1)	4.1 (4), 4.3 (1) ^b	7.4 (2)	13.1 (2)
0.1	2.3 (2)	4.0 (3)

^a $\mu = 1.00$, adjusted with NaClO_4 . Solutions prepared from chloride salt by reaction with AgClO_4 , unless otherwise noted. Reaction followed at 500 $m\mu$, unless otherwise noted. Numbers in parentheses show the number of measurements. ^b Solutions prepared from hydroxoerythro perchlorate. ^c Followed at 490 $m\mu$.

Effect of Chloride Ion on the Cleavage of the Aquoerythro Ion.—When chloride ion was present in the reaction medium, the cleavage reaction of the aquoerythro ion was more rapid than when ClO_4^- was the only anion present, and *cis*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}^{2+}$ was found among the products. Further, the quantity of *cis*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}^{2+}$ found was greater than that expected at equilibrium for the reaction



The concentration of *cis*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}^{2+}$ present in the solution was found to increase initially and then decrease. For example, the quantity of *cis*- $(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}^{2+}$ found in 20 ml of a solution in which total $[\text{Cr}] = 0.014$ *M* and $[\text{Cl}^-] = 0.5$ *M* was 0.005 mmol after 10 min, 0.13 mmol after 40 min, and 0.096 mmol after 120 min, when the cleavage reaction was carried out at 50°.

First-order rate constants, *k*, for the cleavage of the

(18) C. E. Schäffer and P. Anderson in "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., The Macmillan Co., New York, N. Y., 1964, p 571.

aquoerythro ion in $\text{HClO}_4\text{-HCl}$ solutions are shown plotted against chloride ion concentration in Figure 2. The rate constants of Figure 2 were obtained from absorbance measurements at $502\text{ m}\mu$, at which $\text{cis}-(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cl}^{2+}$ and $\text{cis}-(\text{NH}_3)_4\text{Cr}(\text{OH})_2^{3+}$ have identical extinction coefficients, so that decomposition of any $\text{cis}-(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cl}^{2+}$ formed in the reaction to $\text{cis}-(\text{NH}_3)_4\text{Cr}(\text{OH})_2^{3+}$ would not have interfered with the rate measurements. It is seen that k increases steadily with increasing $[\text{Cl}^-]$, the increase being roughly linear in $[\text{Cl}^-]$. The plots of Figure 2 are consistent with a rate law of the form

$$\text{rate} = (k + k'[\text{Cl}^-])[\text{dimer}] \quad (6)$$

where the chloride-independent rate constant, k , should be the same as the rate constant for the same temperature in Table III. Values of k' obtained from the slopes of the plots of Figure 2 are $9.6 \times 10^{-4}\text{ M}^{-1}\text{ sec}^{-1}$ at 60.0° , $1.8 \times 10^{-3}\text{ M}^{-1}\text{ sec}^{-1}$ at 65.0° , and $2.7 \times 10^{-3}\text{ M}^{-1}\text{ sec}^{-1}$ at 70.0° .

A possible explanation for the dependence of the cleavage rate on $[\text{Cl}^-]$ and for the appearance of $\text{cis}-(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cl}^{2+}$ as a product would be that a reactive intermediate is formed by reaction of the aquoerythro ion with Cl^- . When the aquoerythro ion reacted with a $0.5\text{ M HCl-}0.5\text{ M HClO}_4$ solution for 45 min at 50° and the solution was separated on a column of Dowex 50W-X2 resin, a new band was observed on the column. This band separated from the aquoerythro band while $(\text{NH}_3)_5\text{CrOH}_2^{3+}$ was being eluted with 2.5 M HClO_4 , and the new band was eluted with 3 M HClO_4 . The complex in this band contained Cl^- (ca. 0.5 g-atom/g-atom of Cr) and was rather reactive, as judged from the fact that the effluent preceding its elution from the column was colored. The spectrum of this new complex is shown in Figure 3, in which it is designated as the *cis*-chloroerythro ion, for reasons to be discussed later.

Reaction of the Chloroerythro Ion with Hg^{2+} .—When $\text{Hg}(\text{ClO}_4)_2$ was added to a solution of the chloroerythro ion in 1 M HClO_4 , a rapid color change from red-violet to red was observed. When chloroerythro chloride was stirred into a concentrated solution of $\text{Hg}(\text{ClO}_4)_2$ in 1 M HClO_4 , a deep red solution was obtained, and a light red solid precipitated when the solution was cooled and treated with 70% HClO_4 . The spectrum of a solution of this solid is shown in Figure 3, in which it is designated as the *trans*-aquoerythro ion. This so-called *trans*-aquoerythro ion could be precipitated also as the bromide salt.

Discussion

As was noted in the Introduction, there should be two geometrical isomers of both the chloroerythro and the aquoerythro ions, since the nonbridging ligand other than NH_3 could be located either *cis* or *trans* to the bridge. This study has provided good chemical evidence which may be used to assign the configurations of these ions. Garner and coworkers¹⁹ have

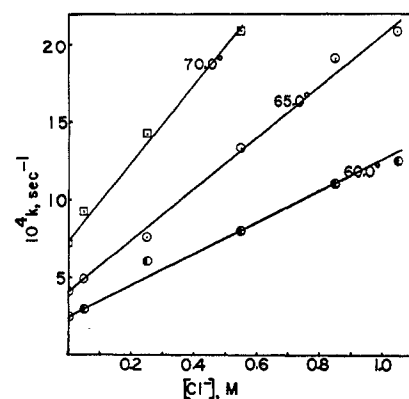


Figure 2.—Variation of the observed first-order rate constant for the cleavage of the aquoerythro ion with chloride ion concentration. Solid lines are least-squares fits of data points. All runs were followed at $502\text{ m}\mu$, ionic strength = 1.0, and $[\text{H}^+] = 1.0\text{ M}$.

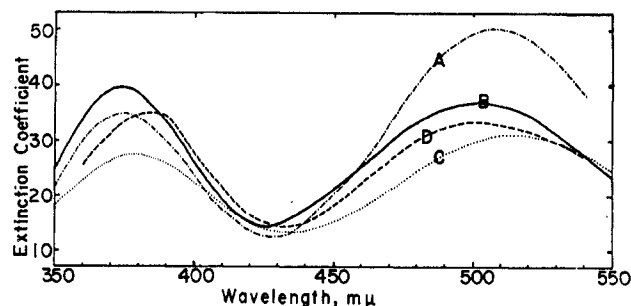


Figure 3.—Spectra of binuclear complexes at 25° in 1 M HClO_4 : A, $\text{cis}-(\text{NH}_3)_3\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4\text{OH}_2^{5+}$; B, $\text{trans}-(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4\text{OH}_2^{3+}$; C, $\text{cis}-(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4\text{Cl}^{4+}$; D, $\text{trans}-(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4\text{Cl}^{4+}$.

shown that the substitution reactions of a large number of dihalo- and haloaquo(bis(diamine)chromium(III) complexes occur with retention of configuration, *i.e.*, *cis* complexes yield *cis* products and *trans* reactants yield *trans* products. Likewise, it has been observed that a number of dihalo- and haloaquotetraamminechromium(III) complexes aquate with essentially complete retention of configuration.²⁰ For example, $\text{trans}-(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}^{2+}$ aquates to form $\text{trans}-(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$, whereas $\text{cis}-(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}^{2+}$ aquates to form $\text{cis}-(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$. In this study we have found $\text{cis}-(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$, but not $\text{trans}-(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$, as the tetraammine product of the cleavage of the aquoerythro ion, under conditions such that $\text{trans}-(\text{NH}_3)_4\text{Cr}(\text{OH}_2)_2^{3+}$ would not have been lost by isomerization or loss of NH_3 . On the other hand, we have found that the cleavage of the chloroerythro ion yields $\text{trans}-(\text{NH}_3)_4\text{Cr}(\text{OH}_2)\text{Cl}^{2+}$ as the major tetraammine product. Assuming that the cleavage reactions occur also with retention of configuration, we assign the *cis* configuration to the aquoerythro ion and the *trans* configuration to the chloroerythro ion.

Further support for these assignments may be ob-

(19) L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).

(20) D. W. Hoppenjans, J. B. Hunt, and C. R. Gregoire, *ibid.*, **7**, 2506 (1968).

tained by examination of Figure 3. In Figure 3 the chloroerythro ion is called the "trans-chloroerythro" ion, the aquoerythro ion is called the "cis-aquoerythro" ion, the species formed by the reaction of the aquoerythro ion with chloride ion is called the "cis-chloroerythro" ion, and the species formed by the Hg²⁺-induced removal of Cl⁻ from the chloroerythro ion is called the "trans-aquoerythro" ion. It is seen from Figure 3 that the short-wavelength maximum of the trans-aquoerythro ion is higher than that of the long-wavelength maximum, whereas the reverse is true for the cis-aquoerythro ion. This relationship between the peak heights has an analogy in the cis- and trans-tetraammine complexes (see Table IV). In both trans-(NH₃)₄Cr(OH₂)Cl²⁺ and trans-(NH₃)₄Cr(OH₂)₂³⁺ the short-wavelength maximum is the higher, the long-wavelength maximum being split in the chloro complex and broadened in the aquo complex. In both cis-(NH₃)₄Cr(OH₂)Cl²⁺ and cis-(NH₃)₄Cr(OH₂)₂³⁺ the long-wavelength band is higher than the short-wavelength band. The analogy between the dimers and the tetraammine complexes is not complete, since the tetraammine fragment constitutes only half of the dimeric molecule, and the effect of the pentaammine fragment should be to make the long-wavelength band the higher. The analogy between the monomers and dimers may be applied also to the chloroerythro dimers. In the trans-chloroerythro ion the short-wavelength maximum is slightly higher than the long-wavelength maximum, whereas the long-wavelength maximum is definitely the higher in the cis-chloroerythro ion. In any event, Hg²⁺-induced replacement of Cl⁻ by H₂O in the chloroerythro ion gives a product different from the aquoerythro ion, from which we must conclude that the chloroerythro and aquoerythro ions have different configurations. The weight of evidence supports the cis configuration for the aquoerythro ion and the trans configuration for the chloroerythro ion.

The two bonds between chromium and the bridging oxygen atom are different in the unsymmetric erythro dimers, and it is interesting to ask which of these bonds is broken when these dimers cleave. In the case of the chloroerythro ion, an answer is provided by reaction stoichiometry. When the chloroerythro ion cleaves in the presence of free chloride or bromide ion, as in the syntheses of trans-(NH₃)₄CrCl₂⁺ and trans-(NH₃)₄CrBrCl⁺, the halide ion from solution is incorporated efficiently into the tetraammine fragment, whereas the pentaammine fragment is found as (NH₃)₅CrOH₂³⁺. Since no formation of trans-(NH₃)₄CrCl₂⁺ from trans-(NH₃)₄Cr(OH₂)Cl²⁺ is observed over a period of several days under similar conditions, these observations imply a strong preference for cleavage of the bond between the bridging oxygen and the tetraammine chromium.

Our results provide also an answer to whether substitution at the bridge or substitution at some other position is the more facile. The formation of trans-(NH₃)₄Cr(OH₂)Cl²⁺ in high yield is evidence that the Cr-O bond (specifically, the tetraammine Cr-O bond) is more labile than the Cr-Cl bond of the chloroerythro

ion. The formation of the species which we have called the cis-chloroerythro ion from the aquoerythro ion is evidence that substitution at the water molecule occurs more readily than substitution at either bond to the bridge in the aquoerythro ion. In the cases of the chloroerythro and rhodo ions, substitution at the Cr-N bonds is certainly much slower than cleavage at the bridge.

A comparison of the data of Tables I-III reveals that the cleavage rates of the three dimers studied decrease in the order trans-chloroerythro > rhodo > cis-aquoerythro, the ratios of rate constants at 60° being about 11.2:7.4:1. The Arrhenius activation energies, calculated from the data of Tables I-III, are 28.7 ± 0.3, 28.7 ± 0.4, and 28.1 ± 0.3 kcal mol⁻¹ for the rhodo, cis-aquoerythro, and trans-chloroerythro ions, respectively. These activation energies are so similar that the differences in reaction rates are obviously due almost entirely to differences in ΔS[‡], rather than ΔH[‡]. At 60°, the calculated values of ΔS[‡] are +4.4, +9.6, and +12.5 cal mol⁻¹ deg⁻¹ for the aquoerythro, rhodo, and chloroerythro ions, respectively. There seems little point in attempting to rationalize the trend in reaction rates in terms of structural differences, since three examples hardly suffice to establish a trend. Judging only from qualitative observations, the cis-chloroerythro ion appears to cleave even more rapidly than does the trans-chloroerythro ion.

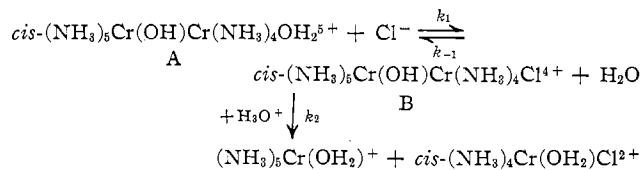
The most likely explanation for the chloride ion catalysis of the cleavage of the aquoerythro ion is that a more reactive intermediate is formed in the presence of chloride ion, particularly since we have been able to isolate the species which we called the cis-chloroerythro ion and have observed that it cleaves much more readily than the aquoerythro ion. We propose therefore the following mechanism for the chloride-

TABLE IV
ABSORPTION MAXIMA AND MINIMA OF
CHROMIUM(III)-AMMINE COMPLEXES^a

Complex	λ, mμ	ε, M ⁻¹ cm ⁻¹
cis-(NH ₃) ₄ Cr(OH ₂)Cl ²⁺	384 (max)	33.3
	439 (min)	9.0
	518 (max)	40.4
cis-(NH ₃) ₄ Cr(OH ₂) ₂ ³⁺	366 (max)	26.6
	419 (min)	7.8
	495 (max)	36.1
trans-(NH ₃) ₄ Cr(OH ₂) ₂ ³⁺	368 (max)	29.7
	415 (min)	10.8
	476 (max)	20.6
trans-(NH ₃) ₄ Cr(OH ₂)Cl ²⁺	383 (max)	39.2
	434 (min)	13.1
	468 (max)	18.2
	506 (min)	14.1
	555 (max)	20.0
trans-(NH ₃) ₄ CrCl ₂ ⁺ ^b	397 (max)	29.9
	447 (min)	13.5
	470 (max)	15.1
	522 (min)	7.3
	591 (max)	25.1

^a In 1 M HClO₄, except trans-(NH₃)₄CrCl₂⁺. ^b In 0.03 M HClO₄.

catalyzed cleavage of the aquoerythro ion



The step which is given the rate constant k_2 would probably be the composite of a slow step and one or more rapid steps, including the neutralization of the OH^- which served as the bridge. If the intermediate *cis*-chloroerythro ion is treated as a reactive intermediate, the general rate law for the reaction by this path is

$$\text{rate} = \frac{k_1 k_2 [\text{A}] [\text{Cl}^-]}{k_{-1} + k_2} \quad (7)$$

Equation 7 is equivalent to the chloride-dependent term of eq 6, where $k' = k_1 k_2 / (k_{-1} + k_2)$. It seems useless to speculate on the relative magnitudes of the rate constants of the proposed mechanism at this time, since we expect to be able to isolate the *cis*-chloroerythro ion and measure its reaction rates directly.

Absorption maxima and minima for the various monomeric complexes synthesized in the course of this study are given in Table IV.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401

Cyanoaquo chromium(III) Complexes. Separation and Identification of the Neutral and Cationic Cyanoaquo Complexes of Chromium(III) and Aquation Kinetics of the Monocyanopentaaquo chromium(III) Ion¹

BY D. K. WAKEFIELD² AND WARD B. SCHAAP

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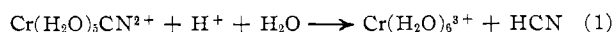
The neutral and cationic cyanoaquo chromium(III) complexes formed as intermediates in the acid-assisted aquation of hexacyanochromate(III) ion were separated using ion-exchange techniques. Species isolated include the uncharged 1,2,3-tricyanotriaquo chromium(III) complex and the *cis*-dicyanotetraquo- and cyanopentaaquo chromium(III) cations. The aquation kinetics of the cyanopentaaquo chromium(III) ion were studied in acidic aqueous solutions and were found to proceed *via* an acid-independent pathway and also an acid-catalyzed pathway involving an equilibrium protonation of the complex. The rate of the aquation is described by the rate law $-dC_t/dt = (k_0 + k_H K_{eq} [\text{H}^+]) C_t / (1 + K_{eq} [\text{H}^+])$, where C_t is the total concentration of the cyanopentaaquo chromium(III) ion in both protonated and nonprotonated forms. At 25° in perchloric acid-sodium perchlorate solutions of ionic strength 2.0 *M*, the rate parameters are $k_0 = (1.1 \pm 0.1) \times 10^{-5} \text{ sec}^{-1}$ for the acid-independent path, $k_H = (3.2 \pm 0.1) \times 10^{-3} \text{ sec}^{-1}$ for the aquation of the protonated species, $K_{eq} = 0.185 \pm 0.006 \text{ l. mol}^{-1}$ (for the protonation equilibrium), and $k_H K_{eq} = (5.90 \pm 0.05) \times 10^{-4} \text{ sec}^{-1} \text{ l. mol}^{-1}$. The aquation was also studied at 15, 35, and 45° and the activation parameters were calculated. For the acid-independent (k_0) pathway, $\Delta H_0^\ddagger = 26.9 \pm 0.3 \text{ kcal mol}^{-1}$ and $\Delta S_0^\ddagger = 8.9 \pm 1.1 \text{ eu}$. For the acid-assisted ($k_H K_{eq}$) pathway, $\Delta H^\ddagger = 20.2 \pm 0.1 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -5.5 \pm 0.3 \text{ eu}$. The pseudo-first-order rate constants calculated from these activation parameters agreed with the experimental values with an average deviation of 1.3%.

Introduction

In acidic aqueous solutions, the hexacyanochromate(III) ion aquates *via* a series of stereospecific reactions to give, finally, the hexaaquo chromium(III) cation.^{1b,2,3} During the aquation the cyanide ligands are replaced by water molecules in a stepwise manner, forming a pre-

viously unknown⁴ series of intermediate cyanoaquo chromium(III) complexes having the general formula $\text{Cr(CN)}_n(\text{H}_2\text{O})_{6-n}^{3-n}$. Under the proper hydrolysis conditions each of these aquation intermediates can be isolated in solution by ion-exchange techniques. This paper describes the separation, identification, and spectral properties of the neutral and cationic intermediates and the aquation kinetics of one of them, the monocyanopentaaquo chromium(III) ion.

The aquation of monocyanochromium(III) ion (eq 1)



(1) (a) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-256 (Document No. COO-256-84). (b) Presented in part before the Division of Inorganic Chemistry at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; at the 9th International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, Sept 1966; and at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

(2) Taken in part from a thesis submitted by D. K. Wakefield to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree in chemistry, 1967.

(3) (a) R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967); (b) R. Krishnamurthy, Thesis, Indiana University, 1966.

(4) (a) The cyanopentaaquo chromium(III) complex was prepared by a different method and previously reported by J. H. Espenson and J. P. Birk, *J. Am. Chem. Soc.*, **87**, 3280 (1965). (b) A method of preparing cyanopentaaquo chromium(III) ion at higher concentrations is given by J. P. Birk and J. H. Espenson, *ibid.*, **90**, 2266 (1968).