UCRL-11410
c.2

University of California

Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

HYDROLYTIC POLYMERIZATION IN Cr(III) SOLUTIONS

UCRL-11410
c.2

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Research and Development

UCRL-11410

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

HYDROLYTIC POLYMERIZATION IN Cr(III) SOLUTIONS

Sister Gertrude Thompson, C.S.J.

(Ph.D. Thesis)

JUNE 1964

Printed in USA. Price $2.25. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D.C.

HYDROLYTIC POLYMERIZATION IN Cr(III) SOLUTION

Sister Gertrude Thompson

Department of Chemistry
and Inorganic Materials Research Division,
Lawrence Radiation Laboratory,
University of California,
Berkeley, California

ABSTRACT

To establish the formulas of two hydrolytic chromium (III) species, equilibrium measurements of the formation of a dimer, $Cr_2(OH)_2^{4+}$, and trimer, $Cr_3(OH)_4^{5+}$, from monomeric $Cr(H_2O)_6^{3+}$ have been carried out using ion-exchange analytical techniques. The decomposition in acid solutions of the dimer can be followed spectrophotometrically and apparently occurs by way of a singly bridged dimeric intermediate, $CrOHCr^{5+}$. Since appreciable concentrations of the intermediate may be prepared, the rate law for the reverse action - intermediate to doubly bridged dimer - can be readily determined: first order in chromium and predominantly hydrogen ion-independent. At lower acidity - below 0.1 M - the rate data indicate appreciable hydrolysis of the intermediate. In solutions of moderate acidity, the further decomposition of the intermediate to monomer can also be followed and has been found to be first order in chromium and hydrogen ion independent.

Freezing point depressions at the ice-perchloric acid hydrate eutectic have served to establish the dimeric character of the intermediate as well as to confirm the equilibrium results for the formation of the two hydrolytic chromium (III) species.

ESR measurements of three polynuclear species and the monomer were carried out to determine the g value for each species. Following the method

of Kambe, the variation of the magnetic susceptibility as a function of temperature was fitted to a theoretical plot to determine the degree of coupling of spins on adjacent chromium atoms and the nature of the bridging groups. The values reported for J, the exchange coupling constant between chromium atoms, are in substantial agreement with those reported for similar compounds by Earnshaw and Lewis. Comparison with analagous iron (III) dimers indicated that strong π-bonding of the hydroxy groups cannot account for the observed coupling constants and that the results for complexes of both metal ions may better be explained in terms of σ bonding. On the basis of these measurements, the trimer appears to have a linear form.

TABLE OF CONTENTS

Abstract iii

I. Introduction 1

II. Apparatus and Equipment 5

III. Reagents and Analytical Procedure 8

IV. Experimental Procedures 10

A. Equilibrium Constants 14

1. Separation and Analysis 14

2. Experimental Procedure 18

B. Kinetics 21

C. Physical Properties of Hydrolytic Species 25

1. Freezing Point Depression Measurements 25

2. Magnetic Susceptibility 27

3. ESR Measurements of g Values 29

a. Theoretical Derivation 30

b. Experimental Procedure 35

V. Results and Discussion 36

A. Determination of Equilibrium Constants for the Formation of Two Polymers from Monomeric Hexaquochromium (III) 36

1. Experimental Results 38

2. Discussion 43

B. Kinetics of the Interconversion and Decomposition of the Dimeric Species 44

1. Interpretation of Data 44

2. Discussion of Results 51

3. Attempts to Isolate the Intermediate 66

4. Formation of the Dimer by Oxidation of Chromium (II) Solutions 67

C. Characterization of Polymeric Species 70

1. Determination of Degree of Polymerization by Freezing Point Depression Measurements . . . 70

2. Measurement of Variation of Magnetic Susceptibility with Temperature 72

a. Theoretical Treatment of Data 72

3. ESR Measurement of g Values 91

4. Attempts to Prepare Crystals 93

Acknowledgments 95

Figure Captions 96

References 97

I. INTRODUCTION

Since the second World War, the field of aqueous solutions of inorganic compounds has been a fertile one, producing interesting investigations in many directions. Metal ion complexes, in particular, have been studied most closely with respect to the kinetics and mechanism of their formation and the equilibria occurring in such solutions. Ligand field theory has been developed and applied to the complex of problems uncovered in the course of research in the hope of providing a theory central to their understanding.

Several of the investigations have centered on the nature of the metallic ions themselves when dissolved in water and complexes derived from them. Indeed, many conventional hydrolysis studies seem to require the existence of polymeric species to account for the experimental data; Sillen[1] among others has stressed the importance of this consideration. In fact, simple hydrolysis, polymerization of hydrolysis products, successive hydrolysis of the polymers themselves, ion-pair formation - all these factors tend to occur in solutions to a greater or less extent and to make it difficult to disentangle the influence of one individual factor from that of another in the morass of data.

Somewhat different approaches have been attempted to resolve the difficulties: ultracentrifugation has been used;[2] light-scattering methods, magnetic susceptibility measurements, and ion-exchange techniques, applied to appropriate systems, leave no doubt that such species do exist and are quite prevalent, particularly for highly charged or small ion and under conditions of low acidity;[3,4,5] pH measurements using various techniques have been most commonly used to study such systems.[6] When the spectra of various species are known and they are found to be sufficiently different in some region,

then spectrophotometric methods can be used.[7] Conductometric and NMR measurements have also been used to investigate these systems.[8,9]

In most cases studied the solutions represent a mixture of species and the data correspondingly reflect uncertainties with respect to statements about individual complexes. Equilibrium constants are not easily obtained nor are details of the structure of hydrolysis products. Systems of inert complexes, i.e. those for which substitution reactions do not reach equilibrium within the time of mixing, as defined by Taube,[10] can however be studied and kinetic methods as well as a number of equilibrium methods can be called upon to yield stability constants. Among such systems which have been most widely studied are octahedral complexes of d^3 and spin-paired d^4, d^5, and d^6 metal ions, all of which have been predicted to be inert by both ligand-field and valence-bond theory.

Chromium (III) complexes present an opportunity for study and have accordingly been the object of considerable research. N. Bjerrum in the early part of this century used EMF measurements to investigate the hydrogen ion concentration in solutions of Cr(III) of varying composition.[11] After correcting for hydrolysis of the monomer, he attempted to explain the hydrogen ion concentration in terms of the formation of polymerized species. He assumed certain degrees of hydrolysis to produce these species and then tried to correlate the variation of their concentrations with monomer in equilibrated solutions, to infer the degree of their polymerization. The degree of hydrolysis assumed for the species present were one, two and 2.5 OH^- per Cr, and the corresponding degree of polymerization 2,6, and 12, thus producing the species $(CrOH)_2^{4+}$, $(Cr(OH)_2)_6^{6+}$, and $(Cr(OH)_{2.5})_{12}^{6+}$. He reported equilibrium constants for their formation, although it was impossible to ascertain both the degrees of hydrolysis and polymerization simultaneously and unambiguously.

Since Bjerrum's work, a number of other investigators have reached the same conclusion about the formation of a binuclear complex. Stiasny and Balanyi[12] postulated the formation of "ol" complexes in basic chromium (III) chloride solutions used in tanning and cited in particular the complex $(H_2O)_4\ Cr\langle^{OH}_{OH}\rangle Cr(H_2O)_4^{4+}$ as an explanation for the increase in acidity upon heating or aging of the tanning liquors. To account for the change in pH as a function of dilution in solutions of chromium (III) nitrate containing 0.50 equivalents of potassium hydroxide and also 1M in potassium nitrate, Schaal and Faucherre[13] proposed a two-fold condensation of the chromium to form the complex Cr_2O^{4+}.

In the course of some cryoscopic work in saturated solutions of potassium nitrate, Souchay[14] found that the depression of the freezing point by chromium (III) nitrate solutions, to which potassium hydroxide had been added in a less than one-to-one mole ratio, could best be explained by the presence of a chromium species having the formula $Cr_2(OH)_2^{4+}$.

Hall and Eyring[15] noted that chromium (III) nitrate solutions become acidic upon heating and apparently contain more than one chromium species. They postulated that some of these species could be represented as oxygen-bridged complexes since there were fewer than six waters bound to chromium as determined by their measurements.

More recently, Laswick and Plane[16] and Finholt[17] have succeeded in isolating individual hydrolytic species by ion-exchange techniques from refluxed chromium (III) nitrate and perchlorate systems. Three different species were characterized; 1) a purple monomer, $Cr(H_2O)_6^{3+}$; 2) a blue polymeric species - with a charge of 2+ per chromium and assumed to be either $Cr_2(OH)_2^{4+}$ or Cr_2O^{4+} since species of both kinds are known for chromium dimers; and 3) a green polynuclear species - assumed to be trimeric,

either $Cr_3(OH)_4^{5+}$ or $Cr_3O_2^{5+}$, with a ratio of 4 OH^- groups to 3 Cr(III) atoms. The charge-per-species experiments of both groups of investigators were inconclusive for the polymers, but subsequent work of Ardon and Linenberg[18] using freezing point depressions in 41.7% perchloric has established the dimeric character of what they assume is a sample of blue species only. The oxidation product of aqueous Cr(II) perchlorate solutions has been established as identical to the blue species[19] and it is with this material that Ardon and Linenberg worked. Plane and Kolaczkowski[20] have interpreted their work with O^{18}-enriched water to prove that the bridging group in this same species is not an oxygen bridge but rather two hydroxy bridges.

It was decided to investigate these polymeric species more closely; in particular to measure the equilibrium constants between the monomeric and polymeric forms of hydrolyzed species; to study the kinetics of the decomposition of the blue dimeric species, reported by Finholt[17] to be a two-step process; and to characterize these polynuclear species more completely by learning something more of their structure and manner of formation. Thus, the work reported here consists of 1) the equilibrium between Cr(III) and two of the polynuclear species; 2) the kinetics of decomposition of the dimeric species in acid solution; and 3) the characterization of some of the polynuclear species existing in solution.

II. APPARATUS AND EQUIPMENT

Absorption spectra were measured on a Cary recording spectrophotometer; both Model 11 and Model 14 were used. The wavelength scales were calibrated by checking the emission spectra from hydrogen and mercury discharge lamps. The absorption spectrum of a particular substance was obtained by recording the spectrum of the solution in a quartz cell versus air, then measuring the absorbance of the same cell containing a blank solution versus air, and subtracting the absorbance of the blank to yield the absorbance of the substance in solution.

Kinetic data were also obtained using the Cary spectrophotometer, the cell compartment and/or water-jacketed cell holder being maintained at constant temperature for the duration of the run. The solution samples were contained in closed quartz cells, preheated or cooled to the temperature to be used throughout the kinetic run. For such a run, the instrument was set at a specific wavelength (2700 Å) and the change in absorption followed with time. Solutions themselves were preheated or cooled before injection of the sample into either the cell itself or into a beaker maintained at the same temperature.

Magnetic susceptibility measurements were made using a water-cooled magnet from Spectromagnetic Industries (Model 4-100) and a Mettler balance equipped with a Vernier gauge enabling readings to be made to the nearest 10 micrograms. A simple Guoy tube was used for the measurements; it was calibrated by making measurements with an aqueous solution of nickel chloride (23.88% nickel by analysis). An aluminum chain was attached to the pan of the balance and the tube suspended from this between the poles of the magnet. Four-inch cylindrical pole caps were used in all measurements

at a sufficient distance to accommodate the tube itself or a hollow Pyrex condenser in which the Guoy tube could be freely suspended. The condenser was used to maintain a constant, fixed temperature within the cavity; the tube was calibrated under these conditions as well. An external water bath was used as a temperature reservoir.

Freezing point determinations were carried out in Dewared cells similar to those described by McMullan and Corbett.[21] The double-walled cell, to which 10.00 cc of the solution was added, was cooled by being immersed in a bath of ethyl alcohol and dry ice (-78.5°C) contained in a second Dewar. The solution was stirred by means of a small Teflon- or glass-coated stirring bar. A Veco thermistor (#32A11) was used for the temperature measurements during which time it was kept in a small, thin-walled glass well filled with petroleum ether, in thermal contact with the solution. Resistance measurements were made using a Leeds and Northrup Wheatstone bridge (Test Set #5305), a Honeywell galvanometer (Model 104W1), and a 1.5 volt external battery. The thermistors used were calibrated with an alcohol thermometer and checked against a thermocouple to take into account stem-warming.

Hydrogen ion concentrations in the low-acidity kinetics experiments were checked on a Beckman Model G pH meter standardized against 1.00×10^{-2} M perchloric acid in 2M $LiClO_4$ in a few instances, but were determined by titration with standard base for all runs, of both low and high acidity. A salt bridge consisting of NaCl-saturated agar was prepared in a fine-pore, sintered glass tube, 7 cm in length, 5 mm in diameter at the lower end and widening to 2.5 cm at the top.. The top of the tube was filled with a saturated KCl solution into which the calomel reference electrode was placed. This measure was called for because a precipitate of potassium perchlorate is formed when the calomel electrode is placed directly into perchlorate

solutions and the pH readings obtained are correspondingly irreproducible and inaccurate.

For the equilibrium measurements a small insulated copper block was maintained at constant temperature by water from the temperature reservoir circulating through the block. Three wells in the vessel held 100 cc, tall-form rimless beakers fitted with Lucite tops into which three holes were drilled to fit snugly a thermometer, glass electrode, and salt bridge respectively. The glass electrode was kept at the temperature of the solution to be measured for at least 24 hours prior to measurement and the beakers into which the equilibrated solutions were placed, preheated. pH measurements were made at that temperature, after calibration of the instrument with a pH 4.00 buffer held at the same temperature. The rapidly quenched solutions were later rechecked for consistency against a Beckman Research pH meter, calibrated with a chilled pH 4.00 buffer, all at 0.8°C.

III. REAGENTS AND ANALYTICAL PROCEDURE

A stock solution of chromium (III) perchlorate was prepared by reducing CrO_3 with 30% hydrogen peroxide in the presence of excess perchloric acid. Chromium (II) perchlorate was prepared by passing some of this stock solution through a Jones Reductor into a nitrogen atmosphere, following Finholt's procedure.[17] Most of the ion-exchange separations of chromium (II) oxidation products were carried out using Dowex 50W-X8, 200-400 mesh, AG, cation-exchange resin. The resin was obtained from Bio Rad Laboratories, Richmond, California. Refluxed solutions were also separated on Dowex resins: 50W-X4 and 50W-X2, 200-400 mesh, AG, cation-exchange resin.

A stock solution of sodium perchlorate was prepared by treatment of AG sodium carbonate with a small excess of perchloric acid and the solution then adjusted to a pH of about 6 with sodium hydroxide. A stock solution of calcium perchlorate was prepared by the addition of excess AG calcium oxide to perchloric acid, filtration of the calcium hydroxide precipitate, and final adjustment of the pH to about 6 by the addition of perchloric acid. Concentrations of these species were determined by an ion-exchange technique. A column of Dowex 50 cation-exchange resin was prepared and converted to the hydrogen form by washing with 2M HCl. The column was then washed with water until the pH of the effluent solution was about 5. A known volume of the solution was applied to the top of the column, the displaced hydrogen ions washed from the column and titrated with standard NaOH to determine the number of equivalents of charge.

Lithium perchlorate and calcium perchlorate, obtained from G. F. Smith, were used without further purification.

All perchloric acid solutions were prepared by diluting 70% doubly distilled G. F. Smith perchloric acid. All other chemicals were reagent grade and were used without further purification. Ordinary distilled water was used throughout this work.

Chromium concentrations were normally determined spectrophotometrically as $CrO_4^{=}$ at 372 mμ with $\epsilon = 4.81 \times 10^{-3}$.[22] Chromium (III) was first oxidized to Cr(VI) with excess 30% hydrogen peroxide in alkaline (2M NaOH) solutions. Standards for reference were prepared by diluting weighed, dried samples of potassium dichromate to known volumes with alkaline solutions. Calcium and thorium do not interfere with this procedure. In the equilibrium studies, the chromium (III) concentration was also determined from the known absorbance values of the individual separated species.

IV. EXPERIMENTAL PROCEDURE

For the separation of the individual components of refluxed chromium(III) perchlorate solutions the following procedure was used. A column of Dowex 50W-X4, 200-400 mesh, 1.0 cm in diameter and 30 cm in height, was prepared in the hydrogen form by adding the resin as a slurry in 2M hydrochloric acid and washing with water until the effluent was about pH 6. The amount of refluxed solution applied to the column was such that the totality of chromium species occupied only the top 50% of the column. The column was then washed with water and a displacement type of elution was carried out with 1.2N thorium (IV) perchlorate solution in 0.01 M perchloric acid. The thorium (IV) ion is more strongly held by the resin than either the monomer or the dimer and in fact, if the concentration of the thorium perchlorate solution is stepped up, more strongly even than the green polynuclear species - thought to be a trimer - which is then displaced in front of the thorium (IV) ion as it moves down the column. The eluting solution does not appear in the effluent until most of the green polynuclear species has been displaced from the column. Each sample then consists of a single chromium (III) species and some hydrogen ion from the eluant. This technique can be used to obtain pure samples of each of the three components: the purple monomer which leaves the column first and is of course highest in amount; the blue dimeric species, which is always a minor constituent, following immediately behind the monomer; and the green polynuclear species, usually a larger quantity than the dimer, which is at the top of the resin and is moved most slowly down the resin. Since the resin is not completely clean after elution but still has a green color, presumably higher polymers of consequently higher charge are present and elution of such species would take place more slowly. It should

be noted that only small quantities of the pure polynuclear species can be obtained in this way for further study. The band fronts of each species are sharp but not always flat and in many instances are so badly tipped that the pure blue species is often only a sample of approximately one cc in volume.

The spectrum of each fraction from the column was taken, the chromium (III) concentration determined, and the absorbance per gram-atom of chromium calculated. (See Fig. 1) These spectra were compared with those reported by Laswick and Plane[16] and Finholt.[17] They check well with the spectra reported by Finholt. Laswick and Plane's results have the same general appearance but appear to be uniformly shifted upward in absorbance units. This could be attributable to a constant error in chromium (III) analysis; lanthanum, a foreign ion present as the eluting species in the polynuclear fractions isolated by their procedures, should not interfere in the determination of chromium concentration. The absorbance at the maxima are given in Table I for each of the species as reported by Laswick and Plane, Finholt, and those observed during the course of this work.

To obtain sufficient quantities of the blue dimeric species a modification of the method of Ardon and Plane was used.[19] A Jones reductor was used to prepare chromium (II) perchlorate solutions and the resulting solution was oxidized by bubbling the solution vigorously with oxygen for a period of 30 minutes. The oxidation product was then applied to a previously prepared column of Dowex 50W-X8, 200-400 mesh, washed with water, and the chromium species eluted by displacement with a 1.2N solution of thorium perchlorate. Three bands developed on the column: a small green band, present only in these solutions and from its spectrum identified as $CrCl^{2+}$, preceding the violet band of chromium monomer - about 10% of the total concentration, and

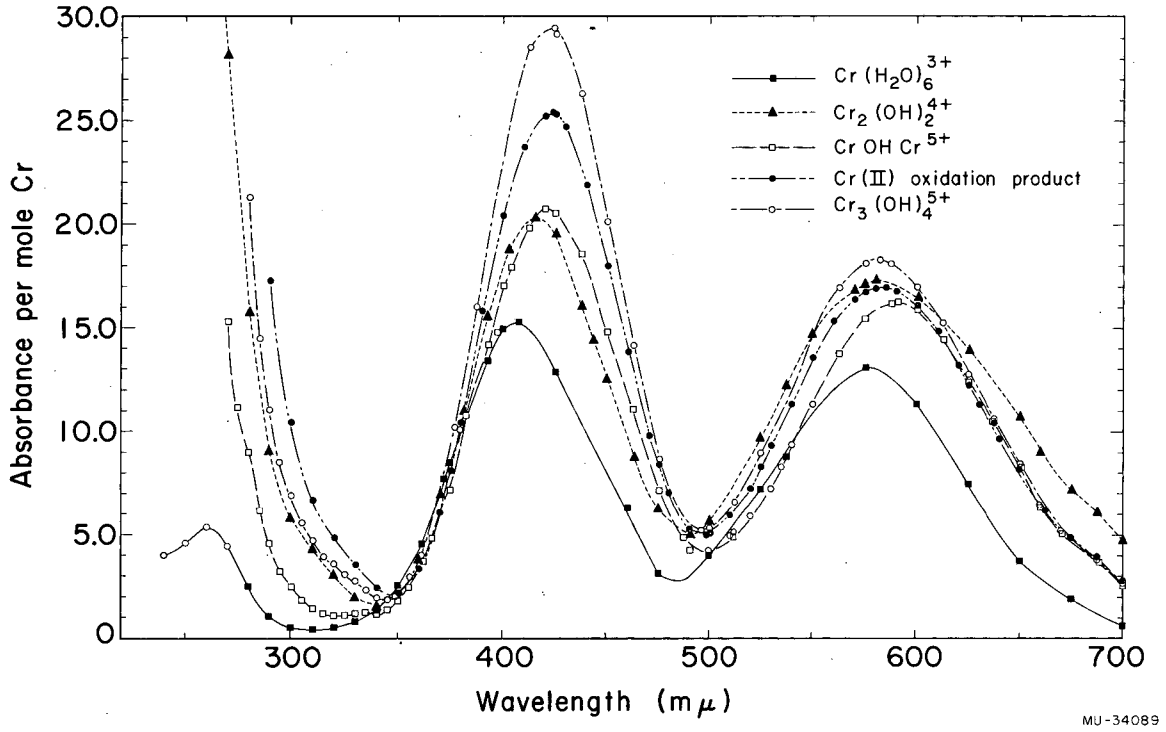

30.0
25.0
20.0
15.0
10.0
5.0
0
Absorbance per mole Cr
300
400
500
600
700
Wavelength (mμ)
Cr (H2O)6 3+
Cr2 (OH)2 4+
Cr OH Cr 5+
Cr (II) oxidation product
Cr3 (OH)4 5+
MU-34089

Fig. 1

Table I. Absorbance at the Maxima of Chromium (III) Species Separated by Ion-Exchange

Species	λ(mμ)		λ(mμ)		Ref.
monomer	574	13.4	408	15.6	(16)
	575	13.1	408	15.3	This work
	582	18.9	418	22.5	(16)
Blue species	580	17.2	416	20.1	(17)
	580	17.3	416	20.3	This work
	580	19.7	426	31.4	(16)
Green Species	582	18.0	424	28.1	(17)
	582	18.2	424	29.4	This work

a dense blue-green band extending to the top of the column immediately behind the monomer. After displacement of these bands, some green-colored chromium (III) species remained strongly absorbed by the resin. When a resin of lower cross-linkage is used, some of this green material is also eluted. Spectra of the green material eluted under these conditions is essentially that of the green polynuclear species. It may be noted that these results show a noticeable deviation from results published by Ardon and Plane, since several chromium (III) hydrolytic species are found to be present among the oxidation products of Cr(II). The only apparent difference in the method of preparation of the two Cr(II) solution lies in the manner of reduction: Ardon and Plane employed electrolytic reduction and the procedure here involved reduction by means of amalgamated zinc, of

necessity producing zinc ions in solution. These latter would not be expected to play any significant role in the oxidative process. The presence of a small amount of $CrCl^{2+}$ can perhaps be explained by the known lability of Cr(II) ions; with the presence of a small amount of chloride in the perchloric acid or on the surface of the zinc amalgam, upon oxidation of Cr(II) to Cr(III), the inert Cr(III) complex would not readily exchange its chloride ligand.

The spectra of three other Cr(III) species are included in Fig. 1: the monomer, hexaquochromium (III), the spectrum of the initial oxidation product of Cr(II), and the spectrum of the substance formed when the blue dimer is introduced into concentrated perchloric acid. The last mentioned will be discussed in the section dealing with the kinetics of the decomposition of the dimer.

All work was carried out using chromium (III) perchlorate solutions to minimize complex formation as completely as possible.

A. Equilibrium Constants

The main problem to solve in the determination of the equilibrium constants for the formation of the polymeric species was one of analysis for the concentration of chromium species and hydrogen ion. The latter was solved by pH measurement. The concentration of the individual chromium species proved more difficult to obtain.

1. Separation and Analysis

There are reported in the literature two different methods for separating hydrolytic chromium species from one another, both employing ion-exchange techniques. Laswick and Plane[16] have found that a series of eluants can be used: 1.0M perchloric acid to elute the monomeric hexaquochromium (III), and two different concentrations of lanthanum perchlorate, 0.02M and 0.20M in

solutions of pH 2, to elute the blue and green polynuclear species, respectively. However, there is question of significant breakdown of the blue fraction sorbed on the column under these conditions of elution: a small band of monomer is eluted ahead of the blue fraction when the 0.02M lanthanum perchlorate solution is being used as the eluant. A second consideration must be given to the length of time the sorbed fractions remain on the resin: the time required to elute successively each of the three species, using different conditions, is of the order of days rather than hours, under the conditions employed in the present work.

The second method, displacement by thorium perchlorate, was developed by Finholt[17] and has been used in the course of this work to obtain samples of pure polynuclear species. The advantage of using displacement rather than elution lies in the fact that none of the displacing agent appears in the fraction collected and the fraction itself is a more concentrated one. Unfortunately the band fronts tend to be badly tipped even under the best of conditions and thus when the blue fraction, a minor constituent in all instances, is collected, it is contaminated with some of the purple fraction preceding it and the green fraction following it. Since the absorbancies of the three fractions do not differ widely from one another at any point in their spectra, individual concentrations of these species within such a mixed fraction cannot be measured accurately. Indeed, if this were not the case, equilibrium measurements could be readily carried out by spectral analysis alone - with the added proviso that these be the only species present; this assumes that other higher polymers or hydrolysis products are not present. Such conditions cannot be assumed, however, since higher polymers have been observed on ion-exchange columns as bands held more tightly than the green polynuclear species and there is

no reason to exclude hydrolysis products under the conditions of acidity present in equilibrated solutions. Further, to achieve a really accurate and clean-cut separation of the species, Finholt used a colloidal form of Dowex 50W-X12- now unobtainable - which of necessity has a very slow flow rate, and as a consequence the ion-exchange separation takes several days. The time factor again calls into question the use of a more selective resin at the cost of longer residence-time on the resin, which may result in changes in the concentration of the different sorbed species by decomposition.

Several additional methods of selectively separating materials adsorbed on a resin by displacement can be suggested. In each instance, the problem is to facilitate the displacement of the initial displacing agent by one stronger than itself, so that successive displacement of the sorbed materials is the end result. In the first method an attempt was made to use the same agent at different concentrations for effecting successive displacements. To do this it is necessary to remove the agent from the column between each pair of displacements. One way of accomplishing this removal is by complexing the eluant cation so that it may readily be replaced by a singly charged cation on the resin column. Since the chromium species were expected to be relatively inert, mercury (II) perchlorate as the displacing agent and chloride ion - in lithium chloride and hydrochloric acid solutions of varying concentration - as the complexing ion were tested. It was found that 1.0M $Hg(ClO_4)_2$ pushed off the purple monomer and just began to elute the other two species. The resin, then saturated with Hg(II) ions, was treated with the chloride solution. At the concentrations tested, the chloride ion was observed to complex all the chromium species as well as the Hg(II). This may be explained in part by the fact

that water molecules are found to be more labile in the presence of an hydroxide ligand on the same metal atom and the chloride ion may complex the polymeric forms more rapidly than it complexes the hexaaquochromium (III).

A second technique can be envisioned in which an anion of the eluant complexes the chromium species itself. While in most cases complexing of chromium (III) is very slow, with a few anions it is rapid. The anion might be something like molybdate ion, used by Hall and Eyring[15] in studies of refluxed chromium (III) nitrate solutions, where the oxygen of the water is presumed to remain attached to the chromium as the molybdate displaces the hydrogen ions of the water.

Another technique that can be employed is successive displacement by a series of cations, all bearing the same charge but differing in radius. This condition is satisfied in a family like the alkaline earths where the elements have a common oxidation state of two and differ only in the size of the cation, the radius increasing as the nuclear charge and electron cloud increases. The charge to radius ratio decreases in the series and Ca(II) < Sr(II) < Ba(II) becomes the observed order of selectivity on a resin. The procedure used is outlined as follows: the monomer is displaced from the resin using calcium perchlorate as the eluant; the concentration of strontium perchlorate is so adjusted that it just displaces the Ca(II) but is only eluting the blue polymer. In principle, this displacement would be continued until the calcium-strontium interface reached the front of the blue polymer band, and then the strontium concentration would be raised to displace the polymer. The process would then be repeated using barium perchlorate to displace Sr(II) and finally the green polymer. In practice, when Ca(II) has been used to displace the monomer

from the resin, it is not pushed from the resin by the Sr(II) before it has succeeded in eluting the blue species. However, calcium perchlorate can be used to achieve separation of the individual species on the resin, since it elutes the two polynuclear species at different rates.

Still another method was suggested by the observation that the individual bands are widely separated on a column of Dowex 50W-X4 after partial elution with calcium perchlorate. The resin was extruded from the column, the sections containing the separated bands cut off and transferred in slurry form to the top of a previously prepared column in the hydrogen ion form. Displacement with thorium perchlorate, it was thought, could then be used to concentrate the material as it comes off the column. Channeling and badly tipped fronts were observed when this was tried. Since the end result was a separated species being eluted by thorium rather than calcium perchlorate, it was decided to continue the study of equilibrated solutions using calcium perchlorate as eluant, in the separation of the species for analysis.

2. Experimental Procedure

A stock solution, 1.0 M in Cr(III), was prepared by reducing CrO_3 with hydrogen peroxide in the presence of an excess of perchloric acid, and determinations of the approximate perchloric acid concentration were made by pH measurement of diluted samples. Sodium bicarbonate in equivalent amount was carefully weighed out and added in small quantities with constant stirring to avoid local excess since the manner of adding a base and the amount added have a pronounced effect on the products formed.[12,13]

Equilibrium studies were carried out with two series of solutions, each with an ionic strength of 1.00 maintained by suitable amounts of sodium perchlorate: the first series had a chromium concentration of

0.10M, the second a chromium concentration of 0.025M. These studies were carried out at three different temperatures: 67.50(±.05)°C, 50.00(±.05)°C, and 37.50(±.05)°C. One hundred cc volumetric flasks were used to contain the solutions and these were placed in a warm-water bath maintained at the appropriate temperature. When the pH of the solution was constant for 24 hours, the solutions were left in the bath for a time period equivalent to that during which they had already been equilibrating and the pH checked again. For the study at 50°C an additional 100 cc of each solution was refluxed for 24 hours, transferred to a volumetric flask and diluted to the mark with distilled water, and allowed to come to equilibrium under the same final conditions.

To test the dependence of the equilibrium constants on ionic strength, another series of solutions was prepared varying in ionic strength from 0.184 to 2.00, but maintaining the same chromium concentration for those solutions below 1.00 in ionic strength.

The pH of all solutions was measured at the temperature of equilibration against a Beckman pH 4 buffer standardized at the same temperature. The values used for the pH 4 buffer at each temperature were as follows: 4.03 at 37.5°C, 4.08 at 50.0°C and 4.12 at 67.50°C.[23] The solutions themselves were then quickly quenched by transferring them to smaller, chilled vessels immersed in an ice-bath. Aliquots of the chilled solution were withdrawn by pipet and applied to prepared columns of Dowex 50W-X4 in the hydrogen ion form. When approximately 10% of the column was loaded with chromium species, elution with 0.50-0.65M calcium perchlorate was begun. In a typical run, a column of Dowex 50W-X4, 1.0 cm in diameter and 37.5 cm in height, was prepared in the hydrogen form and 21.00 cc - in 3.00 cc aliquots - of a solution 0.100 M in Cr(III) was added to the column.

After 40 cc of calcium perchlorate had passed through the resin, the band front of a dense purple fraction, 5.5 cm in length, had moved 24 cm down the column; the front edge of a diffuse blue band, 4 cm in length, was separated from the purple band by a distance of 12 cm, and 4.5 cm from the trailing edge of the blue band was a dense green band, 3.5 cm in length. The resin was colorless in the area between the bands of chromium material and as the elution continued, the separation between the bands increased. The flow rate was kept at 0.5 cc/minute. After 60 cc of calcium perchlorate had passed through the resin, the purple band was completely displaced from the column; the blue band, now 12 cm from the end of the column, was further separated from the still-dense green band and both were being moved down the column. After 170 cc of eluant had passed through the column, all of the blue polymer was eluted and only the green material remained. This in turn was eluted as a single sample. The samples were collected in volumetric flasks of appropriate size and the fractions diluted to the mark. The spectrum of each fraction was taken and the chromium concentration determined using the molar extinction coefficients for the various species reported in this work.

Two columns loaded with samples from each solution were run simultaneously, using a single eluant reservoir for both columns. If samples of the green polymer were left over-night on a column in contact with the eluant, a significant change was observed in the spectrum of the eluted polynuclear species in the near-UV region.

B. Kinetics

The doubly bridged chromium (III) dimer, $Cr_2(OH)_2^{4+}$, decomposes in acidic solutions at a measurable rate according to the net reaction

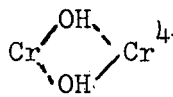
$$Cr_2(OH)_2^{4+} + 2H^+ = 2Cr^{3+} + 2H_2O$$

Finholt[17] observed that in solutions of moderate acidity, ca. 6M $HClO_4$, the absorption spectrum showed a small relatively rapid change, followed by a much slower change to give Cr^{3+}. The investigation of this effect has led to the establishment of the existence of the singly bridged dimeric species, $CrOHCr^{5+}$, and a knowledge of the mechanism of the decomposition of the doubly bridged dimer. The decomposition can be conveniently followed spectrophotometrically since a region where the two complexes are sufficiently different in absorbance does exist: at 2700 Å the absorbance per chromium of the monomer and the dimer are 4.4 and 28.1 respectively. There is no indication that association with the perchlorate ion occurs since no change in the spectrum of either species is observed with increasing perchlorate concentration.

Fresh samples of the blue dimer were prepared for each set of experiments by ion-exchange separation of chromium (II) oxidation products. For the studies in acid media - 1.0 to 7.7 M in perchloric acid - appropriate dilutions of concentrated 70% perchloric were made and the acid solutions thus prepared kept at the desired temperature in a water bath until the chromium solutions were added.

The first series of experiments was designed to follow the over-all decomposition of the dimer to the monomer. It was postulated that the observed two-step process goes by way of a singly-bridged intermediate,

the doubly-bridged dimer breaking one of the bonds to a bridging hydroxy group and the resulting complex simultaneously picking up a hydrogen ion and water molecule from the acid medium, thereby forming an intermediate, $CrOHCr^{5+}$, which in turn slowly breaks down to the monomer, according to the following reactions:



$$Cr^{4+} + H^+ = Cr\text{-}OH\text{-}Cr^{5+} + H_2O \qquad \text{(III-1)}$$

$$H^+ + Cr\text{-}OH\text{-}Cr^{5+} = 2Cr^{3+} + H_2O. \qquad \text{(III-2)}$$

To study this set of reactions, 500 λ portions of fresh dimer were injected into 10.00 cc of acid of varying concentrations, maintained at a fixed temperature and contained in beakers thermostatted at the same temperature - mixed thoroughly, transferred to closed quartz cells, 1.0 cm in length, and the first readings taken within 0.75 minutes. The reaction mixture, contained in cells during the course of a run, was kept at constant temperature in a water-jacketed cell holder within the temperature-controlled sample compartment of the Cary spectrophotometer. The temperature of the cell-holder was assumed to be the temperature of the solution; the same temperature reservoir was used to control the temperature of the initial solutions, the cell-holder and the cell compartment. Kinetic data were accordingly obtained at 15.7, 25.0, 25.5, and 45.0(±.1)°C. No attempt was made to maintain constant ionic strength. The chromium concentration was kept at or near 3.3×10^{-2} M for all runs. A second set of experiments was run to establish the dependence of the reaction on the concentration of the dimer: the chromium concentration was varied by 2-, 5-, and 10-fold factors but the acid concentration was held fixed at 5.7M.

Working from the premise that an equilibrium exists between the two chromium (III) dimers, it was postulated that the equilibrium could be shifted toward the doubly bridged dimer either by diluting or partially neutralizing an acidic solution of the two complexes. Two different procedures were used to test this hypothesis and to obtain kinetic data concerning the reaction between the two species. First, 100 cc samples of fresh dimer were allowed to evaporate in a flash evaporator under reduced pressure to a final volume of 8-10 cc; small portions of the concentrate, nearly 4M in chromium (III), were added to equal volumes of concentrated perchloric acid and allowed to react at room temperature for periods of thirty minutes to an hour. The remaining concentrate was kept at 4°C until used. Samples of the reaction mixture, 6M in perchloric acid, were injected into solutions of lithium perchlorate which were maintained at the desired temperature and contained in quartz cells within the temperature-controlled cell compartment; the concentration of the lithium perchlorate solution was chosen to assure a final ionic strength of 2.00. The solutions were thoroughly mixed and the change in optical density with time recorded. The reaction was studied at 25.0°, 35.5°, and 45.0°C; a few runs were also carried out at 15.7°C. Lithium perchlorate was chosen as the supporting electrolyte since several studies have indicated that little if any change in activity coefficients is observed when lithium perchlorate is substituted for perchloric acid in solutions of constant ionic strength.[24]

The length of the cell to be used was determined from the calculated chromium (III) concentration of the reacting mixture and the degree of change in optical activity which could be conveniently and accurately measured. The range of hydrogen ion concentration in the solutions measured extended from 0.005 to 1.2M. Dependence on the concentration of the

intermediate dimer was determined by maintaining a given hydrogen concentration by the addition of perchloric acid while varying the amount of equilibrium mixture - and hence the chromium concentration - to be added.

The second procedure followed was based upon a reversal of the equilibrium between the dimer and intermediate by a partial neutralization of the solution. Fresh dimer was added to an equal volume of concentrated perchloric acid at room temperature and the resulting solution was allowed to equilibrate for a period of thirty minutes to an hour. 500 λ samples of the product were injected into solutions of sodium perchlorate, contained in preheated beakers and maintained at the desired temperature, and a saturated solution of sodium bicarbonate at the same temperature was run in from a pipete, while the solution was vigorously stirred. As soon as the reaction with sodium bicarbonate ceased, the solution was transferred to a preheated quartz cell, placed in the thermostatted sample compartment and the change in optical density with time recorded. The first readings were obtained within one minute of the initial injection of the equilibrated solution. The same chromium (III) concentration was used in all runs (2.7×10^{-2} M) and the ionic strength of the solutions was maintained at 2.00 by varying the concentration of the sodium perchlorate solution to take into account the amount of added sodium bicarbonate. The same temperature range was covered in this series of runs: 25.0, 35.5, and 45.0 (±.1)°C. As an additional check on the dependence of the rate on the intermediate dimer concentration, dilutions of the equilibrated solution with sodium perchlorate were made to yield solutions of the same final hydrogen ion concentration and ionic strength but varying chromium (III) concentration.

The use of sodium perchlorate in this second series of experiments was dictated by the choice of sodium bicarbonate as a neutralizing agent. Thus to maintain the ionic strength of the solutions at 2.00, sodium perchlorate replaced perchloric acid in these solutions. A check of one of the solutions concentrated by evaporation under vacuum revealed the presence of a small amount of trimer when the material was placed on an ion exchange column. However, later concentrates revealed only the presence of the dimer and small amount of monomer.

C. Physical Properties of Hydrolytic Species

1. Freezing Point Depression Measurements

The determination of the freezing point depression of an eutectic mixture of perchloric acid hydrate and water by what they assume to be the blue species has been carried out by Ardon and Linenberg.[18] This solvent system is a particularly apt choice for the investigation of the chromium (III) polymers since these complexes represent the only foreign ions added to the solvent; the counter-ion perchlorate is already present in the system, as is the hydrogen ion, and therefore neither will affect the freezing point. Thus the freezing point depression depends only on the chromium species present, if it is assumed that the molal freezing point constant K_f is a constant. Since the activity coefficient of the solute is expected to vary only slightly at low concentrations of the solute and the variation itself to be linear,[25] the assumption seems a valid one. The value of K_f was determined by Ardon and Linenberg for a number of metal perchlorates and found to be 4.43°/mole (±7%).

The depression of the freezing point depends only on the number of

particles present; the amount of this depression will be one-half the normal if the chromium (III) ion is dinuclear and one-third the normal if the complex is trinuclear. As Ardon and Linenberg point out, the actual charge of the complex is not a factor and only the number of foreign ions in solution is important; therefore formation of outer sphere complexes does not affect the freezing point even though it may change the charge of the complex.

There are several reasons for repeating the work on the dinuclear complex. Ardon and Plane have established that under their conditions of preparation only one chromium (III) species is present and that it is the same species that has been isolated from refluxed solutions.[19] Thus, for the measurement of freezing point depression, Ardon and Linenberg did not purify the chromium (II) oxidation product but used it as it was prepared. As stated earlier, several chromium (III) species are observed when the Cr(II) oxidation product prepared by reduction with zinc is separated on an ion-exchange column. Even granting that Ardon and Linenberg are using a single species, the conditions of adding the complex to the eutectic solution are such that the actual species being studied is in doubt, since the eutectic has a perchloric acid concentration of 5.27M. With a reported rate of cooling of 0.2°/min, and a total fall in temperature of some 80°C from room temperature, it is doubtful that only the blue species is present; rather, it seems likely that 50-75% of the solution exists as the intermediate. Since it is postulated that the intermediate, too, is a dimer, it would be anticipated that no change in the observed freezing point depression would result. To test this hypothesis, two different methods of preparing the solution for measurement have been employed. To test the assumption that the blue species is a dimer, some of the material is

injected into chilled perchloric acid (-35-40°C) and then cooled the rest of the way to the freezing point. Under these conditions, the material should still remain as dimer. This solution can then be allowed to warm up to room temperature to allow for the formation of the intermediate and be chilled again; or fresh blue material can be injected into the perchloric acid-water solution at room temperature and allowed to equilibrate for a half-hour before chilling. The rate of cooling is much more rapid initially than that used by Ardon and Linenberg so as to avoid formation of monomer. For the study of the trimer, chilled solutions of the perchlorate acid-water mixture are used, the green species is injected with constant stirring, and the solution chilled to the freezing point. Following the suggestion of Ardon and Linenberg, 41.7% perchloric acid rather than the eutectic 40.7% was used in these measurements to increase supercooling and thereby make the detection of the freezing point easier.

2. Magnetic Susceptibility

The magnetic properties of several dinuclear complexes of chromium (III) have been investigated by Earnshaw and Lewis.[26] These complexes are of interest since interaction between the metal atoms is found to depend on both the number and the nature of the bridging groups. Kolaczkowski and Plane[20] have shown that the bridging groups in the blue dimer are hydroxide ions rather than oxygen and one may assume that hydroxides form the bridging groups in the other polymeric species of chromium (III) under investigation in this work. The bond angle in the M-OH-M group also plays a role in the degree of interaction between the metal atoms.

Freshly prepared samples of monomer, dimer, and trimer were prepared from appropriate solutions by ion-exchange techniques: the monomer and

trimer were isolated by displacement of a refluxed solution of 1.0M chromium (III) perchlorate of initially low hydrogen ion concentration - ca. pH 3.5 - from a column of Dowex 50W-X4, 200-400 mesh, with a 0.25M thorium (IV) perchlorate solution; and the dimer by displacement with the same eluant from a column of Dowex 50W-X8, 200-400 mesh. In the latter case the higher cross-linkage is used to hold back any trimeric species that is present. For the dimer preparation a solution of chromium (II) perchlorate through which oxygen had been bubbled for thirty minutes was applied to the column. The intermediate was prepared by a 4- to 5-fold evaporation under vacuum of a solution of fresh dimer in 2M perchloric acid, and subsequent addition of this solution to concentrated perchloric acid. This method of preparation was chosen so that the final chromium (III) concentration would be of the same order of magnitude as that of the other complexes. Fine crystals of monomeric chromium (III) perchlorate were thrown down as soon as the concentrated solutions were mixed. These were separated from the solution by centrifugation and the supernatant was added to a simple Guoy tube.

Measurements were first made on each species at room temperature after flushing the solutions with nitrogen. Table II gives the concentration of each species used and the density of the solution. The density of the solution was determined by weighing some of each sample in a pycnometer at room temperature. The field was maintained at 8000 gauss for these measurements, using four-inch pole caps at a distance of one inch from one another and a current of 6.2 amperes.

For the second set of measurements, a water-jacketed cavity was used to maintain a constant temperature. The Guoy tube was suspended by an

Table II. Concentration and Density of Chromium (III) Species Used in Magnetic Susceptibility Measurements

Complex	Density (g/cc)	Cr^{3+} (M)
monomer	1.10305	0.312
dimer	1.08455	0.371
intermediate	1.66729	0.439
trimer	1.13053	0.740

aluminum chain in the cavity from the pan of a Mettler balance and allowed to come to equilibrium with its surroundings for about an hour or until readings with the field off were constant. The water was circulated through the system from a reservoir held at the desired temperature. The temperature of the cavity, assumed to be the same as the temperature of the sample, was determined by hanging a NBS mercury thermometer in the cavity under the same conditions.

The temperature of the input and output water was also measured and found to differ by 1° on the average; the observed temperature of the cavity was found to lie exactly between these two readings. The pole gap was increased to two inches to accommodate the water jacket and the field was reduced to 6000 gauss at the same amperage (6.2 amperes).

3. Electron Spin Measurements of the g Values

ESR measurements were undertaken to obtain g values for the chromium complexes being studied. An independent measurement of g eliminates one adjustable parameter from the calculation of the variation of χ_A, the atomic susceptibility, with temperature.

The significance of the electron-spin resonance of transition elements

lies in the fact that for these elements with an odd number of electrons, spin angular momentum cannot be zero. Indeed the first transition series behaves as if <u>only</u> spin angular momentum is effective in producing paramagnetism, since orbital angular momentum can be considered to be quenched by the field of the ligands - a field of lower symmetry than that of the free ion - in complexes of these elements.

a. <u>Theoretical derivation</u> - For a paramagnetic ion, the Hamiltonian can be written as:

$$\mathcal{H} = \mathcal{H}_{KE} + \mathcal{H}_C + V + \mathcal{H}_{LS} + \mathcal{H}_M + \mathcal{H}_N \qquad \text{(III-3)}$$

where $\mathcal{H}_{KE} = \sum_k p_k^2/2m$ is the total kinetic energy of the electrons in the paramagnetic ion, $\mathcal{H}_C = \sum_k - Ze^2/r_k + \sum_{j<k} e^2/r_{jk}$ the Coulomb interaction of the electrons with the nucleus and with each other, $V = \sum_k - e_k\phi(r_k)$ the interaction with the ligand field, $\mathcal{H}_{LS} = \lambda\, \underset{\sim}{L}\cdot\underset{\sim}{S}$ the spin-orbit interaction, $\mathcal{H}_M = \beta\, \underset{\sim}{H} \cdot (\underset{\sim}{L} + g\underset{\sim}{S})$ the interaction of the electrons with the magnetic field, and $\mathcal{H}_N = A\underset{\sim}{I}\cdot\underset{\sim}{S}$ a term which includes both the interaction of the electrons with the nucleus (hyperfine interaction) and the quadrupole interaction.

A consideration of the physical picture of the d electrons in the transition elements of the first series shows that they spend most of their time in the outer regions of the ion and therefore tend to experience more powerful interactions with the ligand field than their own spin-orbit coupling. This effect produces nearly complete elimination of the orbital magnetic moment. The small residual effect is related to the ratio of the spin-orbit coupling constant and the magnitude of the ligand field splitting. For this reason, the first transition series does not exhibit spin-only properties, i.e. the splitting factor g varies from

the spin-only value of 2.0023; this variation is itself a measure of the symmetry (and strength) of the ligand field.

The origin of the paramagnetic effect can be related to the concept that an electron spinning on its axis produces a magnetic dipole by its rotation, since it bears a charge. If an external magnetic field $\underline{H}$ is applied, the magnetic dipoles will tend to orient themselves with respect to the field. The interaction with the field can be considered a Zeeman effect and is of the form $\mathcal{H} = g\,\beta\,\underset{\sim}{H}\cdot\underset{\sim}{S}$ where H is the applied magnetic field, S the total spin, β the Bohr magneton and g the splitting factor.

For chromium (III) monomer with a ground state of $^4F_{3/2}$, the angular momentum properties of the coupled electrons require the combined wave function to transform under rotation as spherical harmonics of order 3; there are seven such harmonic polynomials and examination of these in the presence of a cubic array of ligand field sources shows that they split further into groups of 1 + 3 + 3. For elements with less than half-filled shells like chromium (III), the singlet orbital level is the lowest in a field of cubic (octahedral) symmetry. Under the influence of an external magnetic field the change in energy from the singlet orbital level to a state of higher energy is governed by the Hamiltonian:

$$\mathcal{H} = \beta\,\underset{\sim}{H}\cdot(\underset{\sim}{L} + g\underset{\sim}{S}) + \lambda\underset{\sim}{L}\cdot\underset{\sim}{S} + A\underset{\sim}{I}\cdot\underset{\sim}{S}\ . \qquad \text{(III-4)}$$

Consideration of individual contributions of terms within the Hamiltonian leads to a spin Hamiltonian:

$$\mathcal{H}_s = \beta(g_{\perp}(S_xH_x + S_yH_y) + g_{\parallel}\,S_zH_z) + A\underset{\sim}{I}\cdot\underset{\sim}{S} \qquad \text{(III-5)}$$

where $g_{\perp}$ and $g_{\parallel}$ include contributions arising from spin-orbit interaction (terms in λH). If second order calculation to terms of order λ^2 as well

as λH are included, the Hamiltonian becomes:

$$\mathcal{H}_s = g_{\parallel} \beta H_z S_z + g_{\perp} \beta(H_x S_x + H_y S_y) + D(S_z^2 - 1/3\, S(S+1)) + A\underset{\sim}{I}\cdot\underset{\sim}{S} \qquad \text{(III-6)}$$

where D is of the order λ^2/Δ (Δ is the ligand field splitting) and is a measure of zero-field dependence. The term $A\underset{\sim}{I}\cdot\underset{\sim}{S}$ may also have directional dependence.

In solutions, however, the spin Hamiltonian can be broken down into two parts, one of which is invariant under rotation and the other which is orientation-dependent and therefore is a random function of time, as the molecule is tumbled about by the molecules of the solvent liquid. If the tumbling motions are sufficiently rapid, the time-dependent terms average to zero and have little effect. Anisotropic g factors are averaged away and the resonance line can be located by the simple Hamiltonian:

$$\mathcal{H} = g\, \beta H_z S_z + A\underset{\sim}{I}\cdot\underset{\sim}{S} \qquad \text{(III-7)}$$

In the system of chromium (III) complexes studied here, no hyperfine interaction was observed although Cr^{53} does have a spin of 3/2 and is present in natural abundance to the extent of 9.54%. Presumably the hyperfine splitting is just broad enough to be obscured by the signal from the Zeeman splitting term and is lost in the resulting resonance spectrum. Even at higher temperature (and therefore narrower line widths) no hyperfine splitting is observed because even a four-fold change in the line width with a 100° change in the temperature yields a signal of comparable width to that calculated for the hyperfine splitting on the basis of the magnetic moment of Cr^{53} and the known splitting and magnetic moment of the observed Mn^{55} splitting.

It seems then that the simplest Hamiltonian describes the system:

$$\mathcal{H} = g\beta H_z S'_z \qquad \text{(III-8)}$$

where S'_z is the z component of the total spin S' of the complex.

The energy level scheme for the dimers of chromium (III) with S' = 0, 1, 2, 3, and a multiplicity of 2S' + 1 is shown in Fig. 2a., and transitions following the selection rules, $\Delta S' = 0$ and $\Delta M_s = \pm 1$, will be observed.

Similar considerations apply to the trimer. However, the lowest energy state will be a quartet since the energy is determined by a combination of S', the total spin, and S*, the sum of the spins on two of the chromium atoms, where S' has values of 9/2, 7/2, 5/2, 3/2, and 1/2 and S* values of 0,1,2,3. Multiplets of each level are produced by 2S' + 1 splittings. Only the multiplet for the lowest state is shown in Fig. 2b in which the energy level scheme for a linear trimer is presented, and transitions follow the selection rules $\Delta S^* = 0$ and $\Delta M_s = \pm 1$.

Thus if $E'_H = E_o - 3/2\ g\beta H$ and $E''_H = E_o - 1/2\ g\beta H$ for the first allowed transition in the trimer, then $E''_H - E'_H = -\ g\beta H$. If ν is the frequency absorbed in the transition resulting in an energy change, then $E''_H - E'_H = h\nu$, and $h\nu = -g\beta H$. Since ν and H can be measured quite precisely, g may be readily determined. Similar calculations apply to the dimers of chromium (III) as well as to the monomer.

It should be pointed out that the E_o's for the polynuclear species are not the same from one energy level to the next since the Hamiltonian includes another term:

$$\mathcal{H} = -\ 2J\ \underset{\sim}{S}_1 \cdot \underset{\sim}{S}_2 \qquad \text{(III-9)}$$

for the dimeric species and

$$\mathcal{H} = -\ 2J(\underset{\sim}{S}_1 \cdot \underset{\sim}{S}_2 + \underset{\sim}{S}_2 \cdot \underset{\sim}{S}_3) \qquad \text{(III-10)}$$

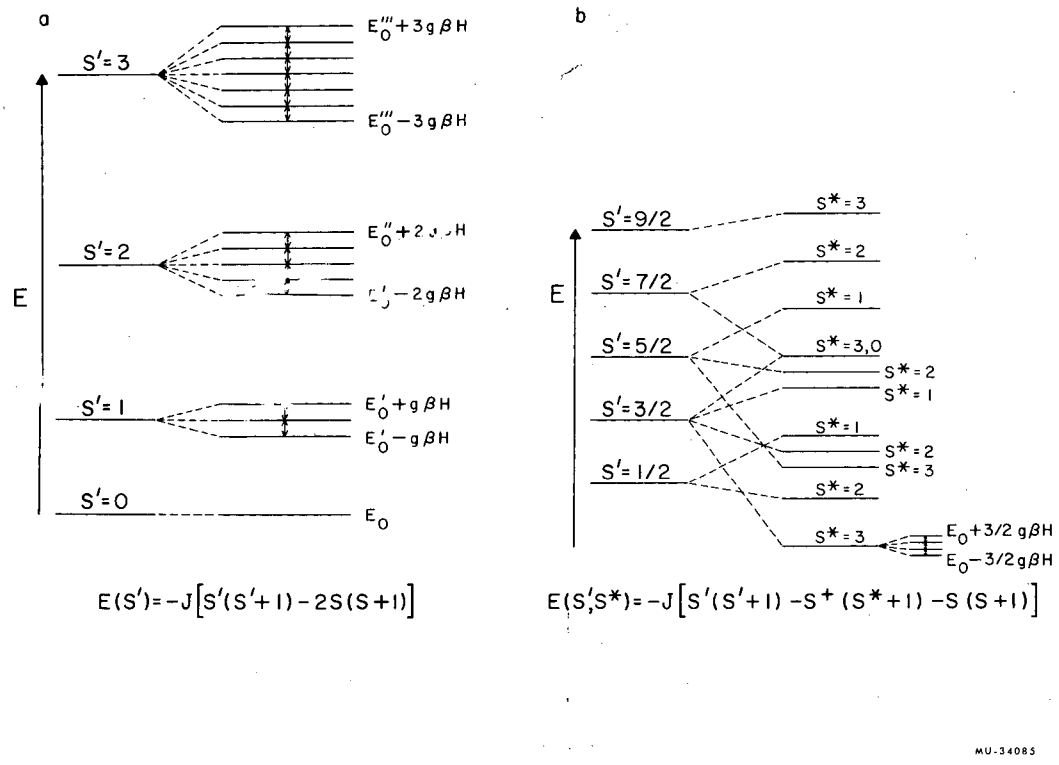

a
S′=3
S′=2
S′=1
S′=0
E
E′′′0+3gβH
E′′′0−3gβH
E′′0+2gβH
E′0−2gβH
E′0+gβH
E′0−gβH
E0
b
S′=9/2
S′=7/2
S′=5/2
S′=3/2
S′=1/2
S*=3
S*=2
S*=1
S*=3,0
S*=2
S*=1
S*=1
S*=2
S*=3
S*=2
S*=3
E0+3/2 gβH
E0−3/2gβH
E(S′)=−J[S′(S′+1)−2S(S+1)]
E(S′,S*)=−J[S′(S′+1)−S+(S*+1)−S(S+1)]
MU-34085

Fig. 2

for the trimeric, as indicated in Section V.C.2. In fact, it is only because J has a small value that ESR spectra can be observed at room temperature for the dimeric species: the energy difference between the ground state and the next level is 2J where J is the exchange interaction and is quite small (7.5° and 16°) for the two dimeric species.

b. Experimental procedure - Samples of monomer, intermediate, dimer and trimer were taken from solutions prepared for use in the magnetic susceptibility measurements. All spectra were taken with a conventional X-band (9000Mc) ESR apparatus employing various field modulations. Temperatures of the solutions were measured using a very fine Cu-constantin thermocouple; all solutions were run at room temperature. The samples themselves were contained sealed melting point capillary tubing, with the exception of the intermediate which was contained in a flat, thin-walled standard cell from Varian. Magnetic field measurements were made with a proton resonance probe and frequency counter. Spectra were observed in two ways: oscilloscope display and x-y linear display, using a Variplotter 1110 from EAI. Line widths reported refer to the full width at points of maximum slope of the signal and are designated as ΔH. The magnitude of the magnetic field modulation is governed by the factor, ΔH, and since the polynuclear species were observed to have quite broad line widths, considerable variation in modulation was called for, e.g. 100 cps for the monomer and 500 cps for the blue dimer.

V. RESULTS AND DISCUSSION

A. Determination of the Equilibrium Constants for the Formation of Two Polymers from Monomeric Hexaaquochromium (III)

Although several investigators have postulated the existence of a dimer, $Cr_2(OH)_2^{4+}$, and related "ol" complexes to explain the pH dependence and cryoscopic behavior of chromium (III) solutions, there was no separation and identification of individual species until Laswick and Plane[16] and Finholt,[17] working independently found three different chromium (III) species in refluxed solutions of chromium (III) perchlorate: the purple monomer, $Cr(H_2O)_6^{3+}$; a blue species tentatively identified as $Cr_2(OH)_2^{4+}$ or Cr_2O^{4+}; and a green species tentatively identified as $Cr_3(OH)_4^{5+}$ or $Cr_3O_2^{5+}$. It is due to the comparative inertness of chromium (III) complexes that such individual complexes can be isolated. The investigators concluded that the blue species, whether isolated from boiled solutions[17] or prepared by oxidation of chromium (II) perchlorate,[19] contained one hydroxide or half an oxide per chromium, and that the charge per chromium was two. However, the charge per species experiments did not give results consistent with these observations, and consequently the conclusion that the material was truly the species proposed was still in doubt.

Ardon and Linenberg[18] showed by depression of the freezing-point of a perchloric acid-hydrate solution that the blue complex contained two chromium atoms. Under the conditions of their experiment, however, there is question of the stability of the species and thus the validity of the conclusion is held in abeyance.

The green species isolated from boiled solutions of chromium (III) perchlorate has been shown to have four hydroxide groups per three chromium atoms, but the charge per species experiments are inconclusive and to a

limited extent inconsistent with the first measurement.[17]

Thus, although two polymeric species have been isolated, their identification is not complete. It was decided accordingly to measure the equilibrium constant for the formation of the two proposed species in equilibrated chromium (III) perchlorate solutions. If truly constant values are obtained, then the species do indeed exist and their thermodynamic stability can be calculated.

The equilibrium studied were calculated on the following bases:

$$2Cr^{3+} + 2H_2O \overset{Q_{22}}{=} Cr_2(OH)_2^{4+} + 2H^+ \qquad \text{(V-1)}$$

where

$$Q_{22} = \frac{[Cr_2(OH)_2^{4+}][H^+]^2}{[Cr^{3+}]^2} \qquad \text{(V-1a)}$$

and

$$3Cr^{3+} + 4H_2O \overset{Q_{34}}{=} Cr_3(OH)_4^{5+} + 4H^+ \qquad \text{(V-2)}$$

where

$$Q_{34} = \frac{[Cr_3(OH)_4^{5+}][H^+]^4}{[Cr^{3+}]^3} \qquad \text{(V-2a)}$$

Since the initial volume of the equilibrated solution applied to the resin, the total volume of each fraction and its concentration, and the hydrogen ion concentration are known, the equilibrium constants can be calculated and the existence of the proposed equilibria tested through the constancy of the derived equilibrium constants.

The formation of $CrOH^{2+}$ according to the equation

$$Cr^{3+} + H_2O \overset{Q_{11}}{=} CrOH^{2+} + H^+ \qquad \text{(V-3)}$$

was corrected for by using values of 8.1×10^{-4} at 67.50°C, 3.8×10^{-4} at 50.00°C, and 2.5×10^{-4} at 37.50°C for Q_{11}. These values are based on the work of Postmus and King,[22] in solutions of similar composition and ionic

strength.

1. Experimental Results

The solutions used in the equilibration studies were prepared by taking 100.00 cc of a 1.0M chromium (III) perchlorate solution and treating this solution with 13.442 g of sodium bicarbonate, added in small quantities while stirring continuously, to yield a solution of pH ~ 3. 25.00 cc of the resulting solution was transferred to a 1000 cc volumetric flask, 222.50 cc of a 3.63 M sodium perchlorate solution added, and the flask then filled to the mark with distilled water. An additional 50.00 cc of the $NaHCO_3$-treated solution was added to a 500 cc volumetric flask, 33.00 cc of a 3.63 M sodium perchlorate solution added, and the solution made up to the mark with distilled water. The final solutions were therefore 1.00 in ionic strength. 100 cc samples of these solutions were withdrawn as needed and equilibrated in the bath.

To make up solutions of varying ionic strength, 2.50 cc and 10.00 cc of the $NaHCO_3$-treated solution in 100 cc volumetric flasks were diluted to the mark with distilled water, yielding solutions 0.184 and 0.753 in ionic strength, respectively. In some of the later experiments, a solution of ionic strength 2.00 was prepared by treating 40.00 cc of a 1.47 M stock solution of chromium (III) perchlorate with 2.101 g of sodium bicarbonate; then 20.00 cc of the resulting solution was pipetted into a 100 cc volumetric flask, 1.32 cc of 2.73 M sodium perchlorate solution added, and the solution made up to the mark with distilled water.

Aliquots of the chromium stock solution, 2.50 cc in volume, were withdrawn and added to seven 100 cc volumetric flasks. Varying amounts of perchloric acid were added to six of these, and an ionic strength of 100 was maintained with sodium perchlorate. To determine the effective activity

coefficient of the hydrogen ion, γ, in the chromium (III) perchlorate solutions, pH measurements were made and interpreted according to the following relationship:

$$\log^{-1}(-pH) = \gamma\,[H_a^+] + \gamma\,[H_b^+] + \gamma\,[H_c^+] \qquad \text{(V-4)}$$

where $[H_a^+]$ corresponds to the excess hydrogen ion present in the chromium stock solution due to the manner of its preparation and is an unknown although constant quantity (6.07×10^{-2}); $[H_b^+]$ is the amount of hydrogen ion arising from the hydrolysis reaction (V-3), calculated on the basis of $Q_{11} = 1.5 \times 10^{-4}$ at 25.°C:

$$[H_b^+] = [CrOH^{2+}] = \frac{Q_{11}\Sigma[Cr^{3+}]}{[H^+] + Q_{11}}\ ; \qquad \text{(V-5)}$$

and $[H_c^+]$ is the concentration of hydrogen ion added to the solution. Since $[H_a^+]$ is constant in these solutions, a plot of $\log^{-1}(-pH)$ versus $[H_b^+] + [H_c^+]$ should yield the effective γ for the chromium perchlorate solutions of ionic strength 1.00. Table III shows the data that were used to calculate γ. The slope of the line obtained from these data yields a value of 0.98 for γ. The dependence of γ on the presence of chromium polymers is not known but γ is presumed not to vary widely.

Table IV gives the values that have been calculated for the equilibrium constants from the data obtained in these experiments. It can be seen that there is no appreciable dependence upon the ionic strength within the region studied. Such a result may be considered in terms of the activity coefficients of the constitutents:

$$K_{22} = Q_{22}\,\frac{\gamma_{Cr_2(OH)_2^{4+}}\,\gamma^2_{H^+}}{\gamma^2_{Cr^{3+}}} \qquad \text{(V-6)}$$

and

Table III. Determination of Effective Activity Coefficients of the Hydrogen Ion in Chromium (III) Perchlorate Solutions

Sample	Amount of 4.08M $HClO_4$ added (in cc.)	Conc (M)	Amount of 3.63M $NaClO_4$ added (in cc.)	pH measured	(H^+)
1	0.00	0.00	22.20	1.22	.0607
2	0.25	.0102	21.93	1.12	.0763
3	0.50	.0204	21.62	1.04	.0917
4	0.75	.0306	21.38	0.98	.105
5	1.00	.0408	20.80	0.92	.121
6	1.50	.0612	20.52	0.82	.152
7	2.00	.0816M	19.97	0.74	.183

Table IV. Determination of Equilibrium Constants for Formation of $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$.

T(°C)	$[Cr^{3+}]$ (M)	$[Cr(H_2O)_6^{3+}]$ (M)	$[Cr_2(OH)_2^{4+}]$ (M)	$[Cr_3(OH)_4^{5+}]$ (M)	$[H^+]$ (M)	K_{22}	K_{34}	μ
	.029	.0131	.00120	.00194	.00452	1.41×10^{-4}	5.88×10^{-7}	0.201
	.025	.0135	.000925	.00190	.00625	1.94×10^{-4} (±.16)	1.19×10^{-6} (±.12)	1.00
67.50	.100	.0287 .0825	.00393 .00181	.00771 .00975	.00653 .0251	1.88×10^{-4} (±.17)	1.08×10^{-7} (±.68)	1.00
	.294	.137	.00983	.0217	.0198	1.80×10^{-4} (±.28)	1.40×10^{-6} (±.40)	2.00
	.025	.0160	.0102	.00175	.00379	5.67×10^{-5} (±.26)	8.9×10^{-7} (±2.2)	.184
	.025	.0234 .0209	.00311 .000926	.0019 .00527	.00916 .00496	5.78×10^{-5} (±.37)	1.62×10^{-7} (±.62)	1.00
50.00	.100	.0642 .0888	.00416 .00197	.00660 .00396	.00762 .0152	5.68×10^{-5} (±.29)	2.09×10^{-7} (±.97)	1.00
	.100	.0693	.00470	.00695	.00740	5.34×10^{-5} (±.29)	6.23×10^{-8} (±.23)	.741
	.025	.0600	.00073	.0013	.00302	2.61×10^{-5}	2.65×10^{-8}	.184
37.50	.025	.0139	.000844	.00164	.00263	2.90×10^{-5} (±.19)	3.25×10^{-8} (±.41)	1.00
	.100	.0640	.00325	.00618	.00622	2.87×10^{-5} (±.21)	2.51×10^{-8} (±.24)	1.00

$$K_{34} = Q_{34} \frac{\gamma_{Cr_3(OH)_4^{5+}} \gamma^4_{H^+}}{\gamma^3_{Cr^{3+}}} \qquad \text{(V-7)}$$

The exact dependence of the activity coefficients in solutions of high ionic strength, as is the case here, and with ions of such high charge is unknown. For low ionic strengths the expression:

$$\log \gamma \cong - A Z^2 I^{\frac{1}{2}} \qquad \text{(V-8)}$$

where Z is the charge on the individual chromium complex, A a constant for the solvent at a given temperature, and I the ionic strength of the medium, can be used to express the relationship to charge and ionic strength. It can be seen that for the individual equilibria being reported, the following relationship will then hold:

$$\log \frac{\gamma_{Cr_2(OH)_2^{4+}} \gamma^2_{H^+}}{\gamma^2_{Cr^{3+}}} = -16AI^{\frac{1}{2}} - 2AI^{\frac{1}{2}} + 18AI^{\frac{1}{2}} = 0 \qquad \text{(V-9)}$$

and

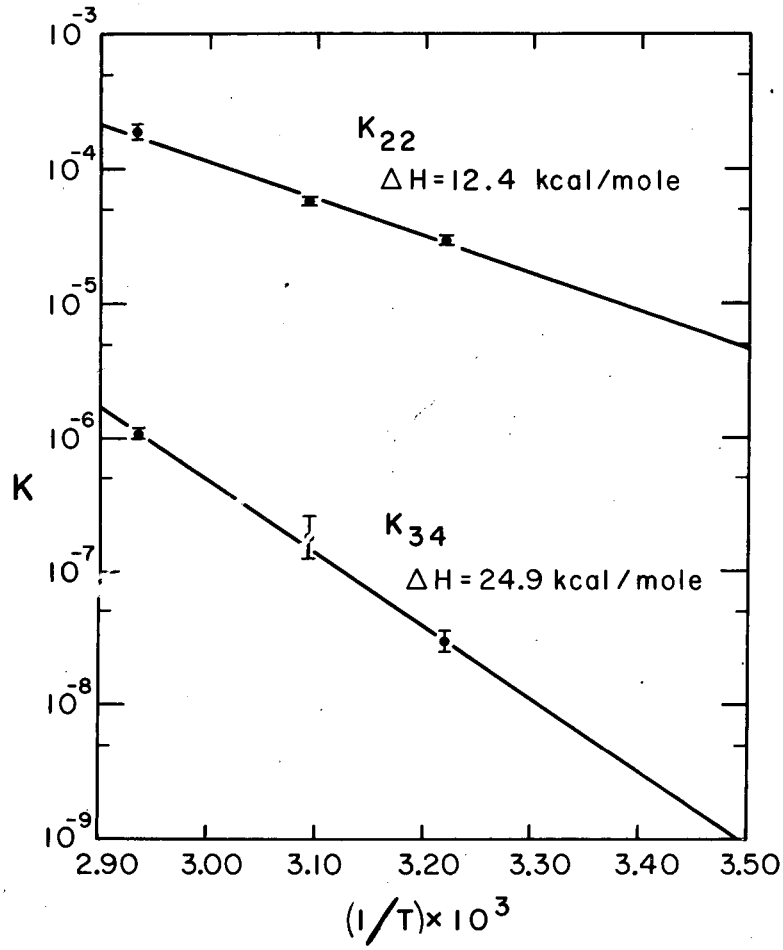
$$\log \frac{\gamma_{Cr_3(OH)_4^{5+}} \gamma^4_{H^+}}{\gamma^3_{Cr^{3+}}} = -25AI^{\frac{1}{2}} - 4AI^{\frac{1}{2}} + 27AI^{\frac{1}{2}} = -2AI^{\frac{1}{2}}. \qquad \text{(V-10)}$$

Thus using this very crude approximation, no ionic strength dependence is anticipated for reaction (1) and only a small dependence in (2). It should be stressed that no great significance can be attached to calculations such as these since the Debye-Hückel limiting law cannot be applied with any degree of certainty in such concentrated solutions as used here.

From a plot of log K versus 1/T, the value of ΔH may be determined for the two reactions (See Fig. 3):

$$2Cr^{3+} + 2H_2O = Cr_2(OH)_2^{4+} + 2H^+ \qquad \text{(V-1)}$$

$$\Delta H = 12.4 \text{ kcal/mole}$$



MU-34077

Fig. 3

$$3Cr^{3+} + 4H_2O = Cr_3(OH)_4^{5+} + 4H^+ \qquad (V\text{-}2)$$

$$\Delta H = 24.9 \text{ kcal/mole.}$$

Using these values $\Delta S_{298°}$ was calculated for each of the reactions, yielding values of 19 e.u. for Eq. (V-1) and 46 e.u. for Eq. (V-2).

Bjerrum[11] has reported a values of 15.4 kcal/mole for the ΔH of the first reaction from his EMF measurements, and a ΔS of 15 e.u. may be determined using his data. Perhaps the ambiguity in the treatment of his data, which requires estimation of both the degree of polymerization and the degree of hydrolysis can explain the discrepancy, since the K's were corrected for the concentration of two polymers which have not been shown to exist in chromium solutions. One of his values for K_{22} does lie close to the line drawn through the experimental log K's reported here.

2. Discussion

These results may be compared with those reported by Milburn[27] for the formation of the iron (III) dimer, $Fe_2(OH)_2^{4+}$: $\Delta H = 12.2 \pm 1.0$ kcal/mole ($\mu = 1$, 25°C) and $\Delta S = 28 \pm 5$ e.u. ($\mu = 1$, 25°C). Entropy changes may actually be within experimental accuracy and in any event the smaller size of the Fe(III) ion would be expected to favor the entropy change. Similar trends are observed in the hydrolysis constants (K_1) of the two ions: $\Delta H = 9.4$ kcal/mole and $\Delta S = 14.1$ e.u. ($\mu = 0$, 25°C) are reported for the reaction:

$$Cr^{3+} + H_2O = CrOH^{2+} + H^+ \qquad (V\text{-}3)$$

by Postmus and King,[22] and Milburn[27] reports $\Delta H = 10.4$ kcal/mole and $\Delta S = 25$.e.u. ($\mu = 0$, 25°C) for the corresponding reaction of Fe (III). These values again reflect the observation that the $T\Delta S$ term difference

is the important one between Cr(III) and Fe(III) hydrolysis reactions, and that in fact most of the difference in hydrolysis constants is present in this term.

Considered from the viewpoint of what is taking place physically, an entropy increase in reactions (V-1) and (V-2) might result from three factors: 1) the larger positive charge of the polynuclear complexes is spread over a wider area and hence is not so effective in ordering water dipoles in the secondary coordination sphere; 2) there are four and eight fewer water molecules ordered in the primary coordination sphere, assuming an octahedral environment for each chromium, in $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$, respectively; 3) two positive charges have been moved away and the +4 species remaining has its charge spread over two centers. All of these factors contribute to a net positive effect.

It may be noted here that these experiments have not actually established that the complexes formed are hydroxy-bridged, only that a dimer and trimer are formed in solution. Evidence for hydroxy bridging in the dimer has been advanced by Plane and Kolaczkowski[20] and further evidence will be offered in later sections of this work, for hydroxy bridges in both polymers.

B. Kinetics of the Interconversion and Decomposition of the Dimeric Species

1. Interpretation of data

If it is assumed that the first reaction observed in the decomposition of the blue dimer is given by the expression:

$$Cr_2(OH)_2^{4+} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CrOHCr^{5+} + H_2O, \qquad \text{(V-11)}$$

then the rate law can be written as:

$$-\frac{d[Cr_2(OH)_2^{4+}]}{dt} = k_1\ [Cr_2(OH)_2^{4+}][H^+] - k_{-1}\ [CrOHCr^{5+}] \qquad \text{(V-12)}$$

$$= k_1^*\ [Cr_2(OH)_2^{4+}] - k_1\ [CrOHCr^{5+}]$$

where $k_1^* = k_1[H^+]$. If $Cr_2(OH)_2^{4+}$ is present initially - the case in the experiments in perchloric acid media - then at any time t:

$$\ln \frac{[Cr_2(OH)_2^{4+}]\ t - [Cr_2(OH)_2^{4+}]\ \infty}{[Cr_2(OH)_2^{4+}]\ o - [Cr_2(OH)_2^{4+}]\ \infty} = -\ (k_1^* + k_{-1})\ \Delta t. \qquad \text{(V-13)}$$

Since the absorption of the solution at any point is equal to the product of three factors: the concentration of the complex, the length of the cell, and the absorbance per chromium of the complex, i.e.,

$$A = \epsilon\ l\ c. \qquad \text{(V-14)}$$

Then Eq. (V-13) can be rewritten as:

$$\ln \frac{A_t - A_\infty}{A_o - A_\infty} = -\ (k_1^* + k_{-1})\Delta t. \qquad \text{(V-15)}$$

In the series of solutions using equilibrated mixtures of the two dimeric species, and therefore containing both $CrOHCr^{5+}$ and $Cr_2(OH)_2^{4+}$ initially the same rate law given in Eq. (V-12) holds, and at any time t:

$$\ln \frac{[CrOHCr^{5+}]_\infty - [CrOHCr^{5+}]}{[CrOHCr^{5+}]_\infty - [CrOHCr^{5+}]} = -\ (k_1^* + k_{-1})\ \Delta t. \qquad \text{(V-16)}$$

When the reaction in acid solution is allowed to continue, the second step of the process results in the formation of monomer, and the experimental results (infra) reaction can be described by the following reactions:

$$CrOHCr^{5+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cr^{3+} + CrOH^{2+} \qquad \text{(V-17)}$$

$$CrOH^{2+} + H^+ \underset{}{\overset{1/K_H}{\rightleftharpoons}} Cr^{3+} + H_2O \qquad \text{(V-18)}$$

$$-\frac{d[CrOHCr^{5+}]}{dt} = k_2\,[CrOHCr^{5+}] - k_{-2}\,[Cr^{3+}]^2\,K_H/[H^+]. \qquad \text{(V-19)}$$

Under the conditions of the experiment, the reverse reaction was negligible as shown by the equilibrium constant to be discussed later for the single bridged-double bridged equilibrium and the value of K_{22}. Then at any time t,

$$\ln \frac{A_t - A_\infty}{A - A_o} = -\,k_2\,\Delta t, \qquad \text{(V-20)}$$

and the data can be represented by a plot of $A_t - A_\infty$.

Figure 4 shows a plot of typical data obtained for the reaction of the dimer in perchloric acid solution; the reaction was followed over a period of several days. Figure 5 shows a plot of log $A_t - A_\infty$ versus time for the first step in the dimer-acid reaction; the second step can be followed on a similar plot.

Figure 6 shows the change in absorbance with time in a typical run in which the flue dimer is formed from equilibrated solutions of itself and the intermediate in lithium perchlorate solutions, and Fig. 7 shows a plot of log $A_\infty - A_t$ versus time for the same reaction. Deviations from linearity in final stages of the reactions (more than 90% reacted) are sometimes observed in the reactions of the equilibrated solutions, the points falling below the best line through the data. These deviations can be accounted for by formation from the intermediate of some monomer which has a lower molar absorbancy and therefore would make the readings in the final stages seem to decrease more rapidly than anticipated.

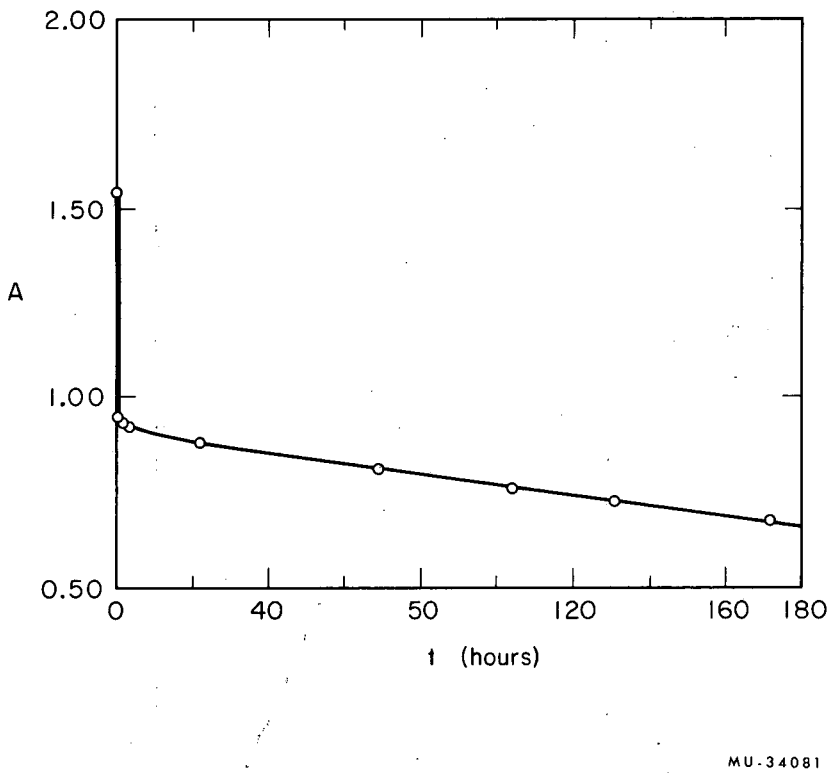


Fig. 4

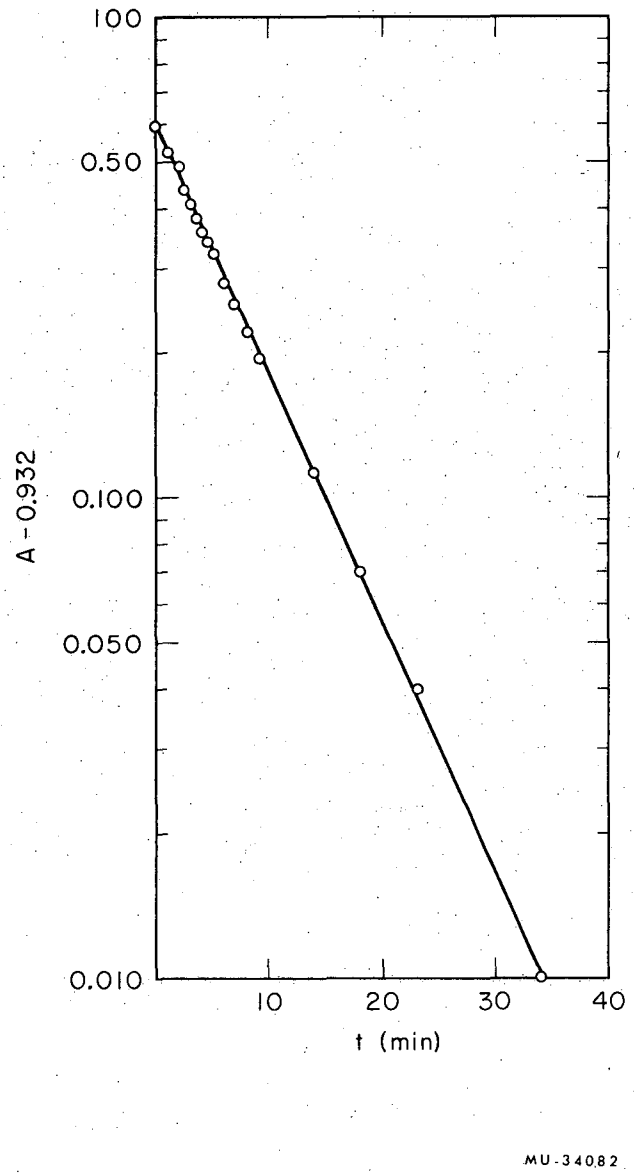
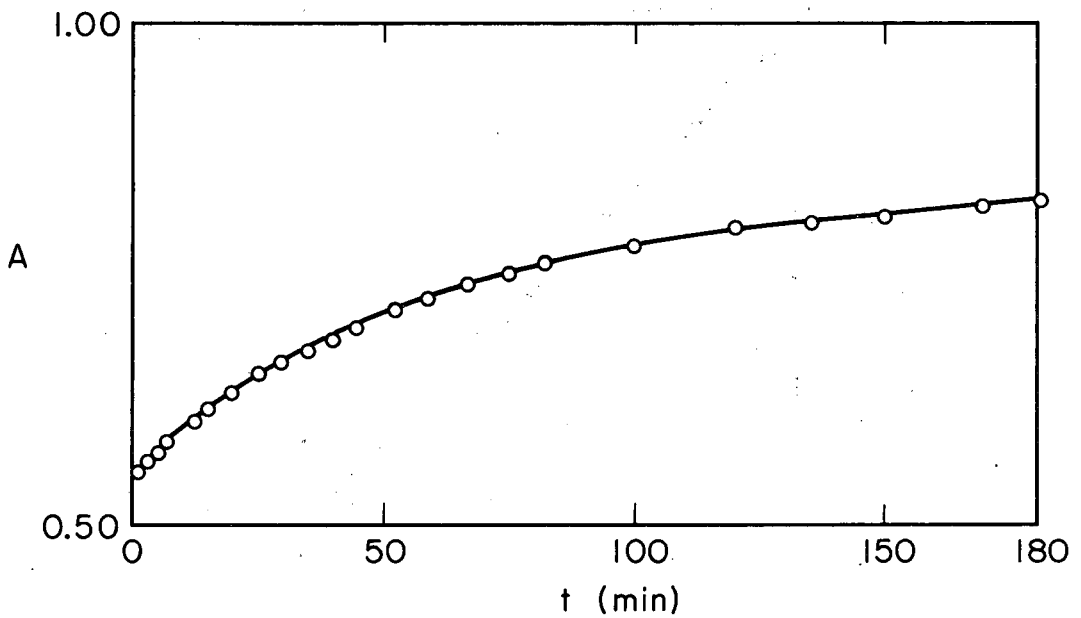
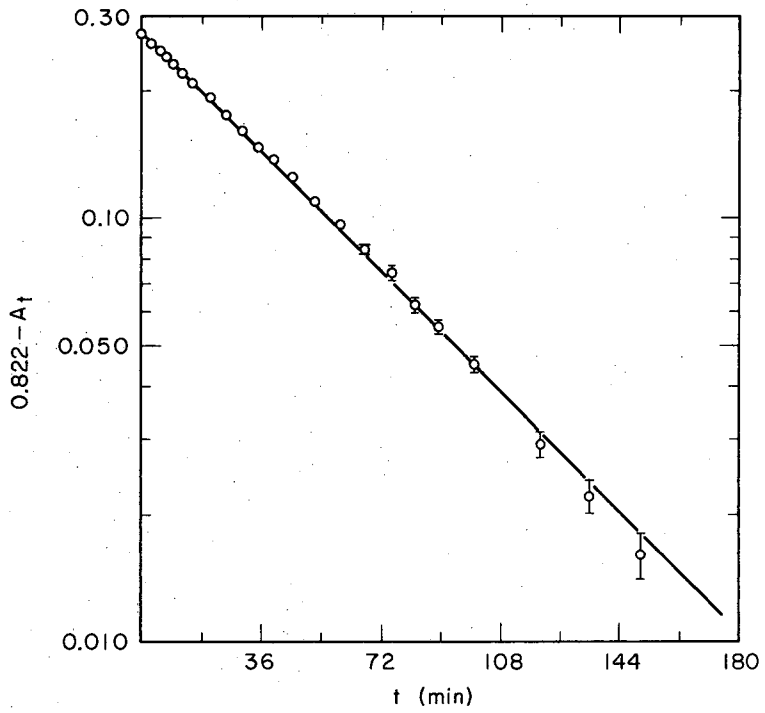


Fig. 5



MU-34080

Fig. 6



MU-34083

Fig. 7

2. Discussion of Results

Figure 8 shows a plot of $k_{observed}$ versus the hydrogen ion concentration for the reactions:

$$Cr_2(OH)_2^{4+} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CrOHCr^{5+} + H_2O \qquad \text{(V-21)}$$

as a function of ionic media and temperature. The data are given in Table V. There are three distinct regions: the region of high acidity, the region of intermediate acidity (0.1 to 2M in perchloric acid), and the region of low acidity.

In the region of high acidity, an examination of the data reveals that the dependence in hydrogen ion concentration is not first order. Such behavior is not unexpected since it might be anticipated that the activity coefficients of the species involved would not be independent of the perchloric acid concentration. Thus:

$$-\frac{d[Cr_2(OH)_2^{4+}]}{dt} = k_1[H^+][Cr_2(OH)_2^{4+}]\frac{\gamma_{H^+}\,\gamma_{Cr_2(OH)_2^{4+}}}{\gamma^{\ddagger}} - k_1[CrOHCr^{5+}]\frac{\gamma_{CrOHCr^{5+}}}{\gamma^{\ddagger}} \qquad \text{(V-22)}$$

Ion-pair formation between such highly-charged species as the dimeric forms of chromium and perchlorate ion in high concentration may also be a contributing factor since the reactive species may well be ion pairs rather than the simple hydrated complexes. However, Raman spectroscopy of some perchlorates in solution has not revealed the presence of such outer-sphere complexes.[28] Activity coefficients are unknown for these or comparable species - ion-pairs or simple hydrates. An alternative approach is to assume that the activity coefficients of perchloric acid solutions of the same concentration apply without consideration of or correction for the higher polymers or chromium monomer - an hypothesis which is suspect when such highly charged species are present.

Table V. Observed Rate Constants

15.8°C

$HClO_4$ solution (variable μ)

$[H^+]$	$[Cr^{3+}]$	k_{obs} (min^{-1})
7.63 M	3.3×10^{-2} M	5.39×10^{-2}
7.21	3.3×10^{-2}	4.17×10^{-2}
6.92	3.3×10^{-2}	3.99×10^{-2}
5.67	3.3×10^{-2}	3.76×10^{-2}
4.41	3.3×10^{-2}	2.15×10^{-2}
3.40	3.3×10^{-2}	1.22×10^{-2}

$LiClO_4$ (μ = 2.00)

0.261 M	5.1×10^{-2} M	2.79×10^{-3}
0.188	3.5×10^{-2}	3.25×10^{-3}
0.142	2.4×10^{-2}	3.42×10^{-3}
0.109	3.2×10^{-2}	2.96×10^{-3}
0.0427	9.2×10^{-3}	3.98×10^{-3}
0.026	5.1×10^{-3}	4.99×10^{-3}
0.017	3.1×10^{-3}	7.14×10^{-3}

25.00°C

$HClO_4$ solution (variable μ)

$[H^+]$	$[Cr^{3+}]$	k_{obs} (min^{-1}) (1st step)	k_{obs} (hr^{-1}) (2nd step)
8.72 M	3.3×10^{-2} M	1.18×10^{-1}	
7.60	3.3×10^{-2}	1.19×10^{-1}	
6.24	3.3×10^{-2}	8.97×10^{-2}	
	6.5×10^{-2}	9.21×10^{-2}	
	3.3×10^{-2}	8.47×10^{-2}	4.15×10^{-3}
5.76	6.5×10^{-3}	1.02×10^{-1}	4.05×10^{-3}
	1.2×10^{-2}	1.00×10^{-1}	

25.00°C

$HClO_4$ solution (variable μ)

$[H^+]$	$[Cr^{3+}]$	$k_{obs}(min^{-1})$ (1st step)	$k_{obs}(hr^{-1})$ (2nd step)
4.73 M	$3.3x10^{-2}$ M	$4.97x10^{-2}$	$4.51x10^{-3}$
3.38	$3.3x10^{-2}$	$2.93x10^{-2}$	$3.69x10^{-3}$
2.07	$3.3x10^{-2}$	$2.01x10^{-2}$	$5.12x10^{-3}$

$LiClO_4$ (μ = 2.00)

1.02 M	$2.11x10^{-2}$ M	$3.01x10^{-2}$
0.803	$1.1x10^{-3}$	$1.92x10^{-2}$
0.790	$1.4x10^{-3}$	$1.52x10^{-2}$
0.697	$1.6x10^{-2}$	$1.38x10^{-2}$
0.438	$7.3x10^{-2}$	$1.11x10^{-2}$
0.321	$1.05x10^{-2}$	$1.20x10^{-2}$
0.317		$1.07x10^{-2}$
0.273	$1.05x10^{-2}$	$1.15x10^{-2}$
0.213	$3.5x10^{-2}$	$1.56x10^{-2}$
0.152	$1.2x10^{-3}$	$1.49x10^{-2}$
0.123	$5.2x10^{-3}$	$1.68x10^{-2}$
0.0950	$1.05x10^{-3}$	$1.50x10^{-2}$
0.077	$1.91x10^{-3}$	$1.83x10^{-2}$
0.076	$4.53x10^{-3}$	$1.90x10^{-2}$
0.019	$1.45x10^{-3}$	$2.26x10^{-2}$
0.0182	$1.03x10^{-3}$	$1.82x10^{-2}$
0.0160	$2.55x10^{-3}$	$1.89x10^{-2}$
0.0177	$1.28x10^{-3}$	$3.44x10^{-2}$
0.0081	$1.35x10^{-3}$	$2.36x10^{-2}$
0.0051	$8.5x10^{-4}$	$3.76x10^{-2}$
0.600	$2.3x10^{-2}$	$1.33x10^{-2}$
0.217	$2.3x10^{-2}$	$1.43x10^{-2}$
0.0132	$2.0x10^{-2}$	$1.54x10^{-2}$
0.091	$2.3x10^{-2}$	$1.88x10^{-2}$
0.0885	$2.3x10^{-2}$	$1.78x10^{-2}$

$NaClO_4$ (μ = 2.00)

$[H^+]$	$[Cr^{3+}]$	k_{obs} (min^{-1}) (1st step)	k_{obs} (hr^{-1}) (2nd step)
.0797M	2.3×10^{-2}M	1.78×10^{-2}	
.078	2.3×10^{-2}	2.03×10^{-2}	
.075	2.3×10^{-2}	1.79×10^{-2}	
.0745	2.3×10^{-2}	1.97×10^{-2}	
		2.00×10^{-2}	
.0700	2.3×10^{-2}	2.07×10^{-2}	
.069	2.3×10^{-2}	1.92×10^{-2}	
.0608	2.3×10^{-2}	2.27×10^{-2}	
.0483	2.3×10^{-2}	2.38×10^{-2}	
.0437	2.3×10^{-2}	2.20×10^{-2}	
.0372	2.3×10^{-2}	2.56×10^{-2}	
.0233	2.3×10^{-2}	2.75×10^{-2}	
.0146	2.3×10^{-2}	5.38×10^{-2}	
.0119	1.6×10^{-3}	5.98×10^{-2}	

35.5°C

$HClO_4$ solution

6.70 M	3.3×10^{-2} M	2.04×10^{-1}	
5.67	3.3×10^{-2}	1.85×10^{-1}	2.90×10^{-1}(±.09)
4.66	3.3×10^{-2}	1.28×10^{-1}	2.70×10^{-2}(±.06)
3.42	3.3×10^{-2}	7.86×10^{-2}	
2.17	3.3×10^{-2}	5.11×10^{-2}	
1.17	3.3×10^{-2}	4.24×10^{-2}	
1.11	3.3×10^{-2}	5.03×10^{-2}	2.01×10^{-2}(±.10)

35.5°C

$LiClO_4$ (μ = 2.00)

$[H^+]$	$[Cr^{3+}]$	$k_{obs}(min^{-1})$ (1st step)	$k_{obs}(hr^{-1})$ (2nd step)
0.807M	1.58×10^{-2}M	5.07×10^{-2}	
0.78	1.15×10^{-1}	4.12×10^{-2}	
0.635	1.20×10^{-2}	4.77×10^{-2}	
0.624	7.00×10^{-2}	4.43×10^{-2}	
0.186	4.47×10^{-2}	5.29×10^{-2}	
0.160	2.2×10^{-3}	5.40×10^{-2}	
0.103	1.5×10^{-2}	6.67×10^{-2}	
0.0625	8.1×10^{-3}	6.86×10^{-2}	
0.0522	6.5×10^{-3}	8.36×10^{-2}	
0.0410	1.7×10^{-3}	7.12×10^{-2}	
0.0257	3.2×10^{-3}	9.07×10^{-2}	
0.0122	1.0×10^{-3}	1.03×10^{-1}	

$NaClO_4$ (μ = 2.00)

0.813M	3.2×10^{-2}M	5.43×10^{-2}	
0.383	1.7×10^{-2}	5.45×10^{-2}	
0.260	1.9×10^{-2}	5.26×10^{-2}	
0.211	1.9×10^{-2}	5.50×10^{-2}	
0.195	1.9×10^{-2}	5.26×10^{-2}	
0.178	1.9×10^{-2}	4.86×10^{-2}	
0.147	1.89×10^{-2}	6.60×10^{-2}	
0.137	1.89×10^{-2}	6.50×10^{-2}	
0.131	5.7×10^{-3}	7.09×10^{-2}	
0.107	1.9×10^{-2}	7.47×10^{-2}	
0.104	1.9×10^{-2}	6.30×10^{-2}	
0.095	1.9×10^{-2}	7.6×10^{-2}	
0.0838	1.9×10^{-2}	6.41×10^{-2}	
0.0773	1.9×10^{-2}	6.32×10^{-2}	

35.5°C

$LiClO_4$ (μ = 2.00)

$[H^+]$	$[Cr^{3+}]$	$k_{abs}(min^{-1})$ (1st step)	$k_{obs}(hr^{-1})$ (2nd step)
.0690 M	$1.89x10^{-2}$ M	$8.72x10^{-2}$	
.0650	$2.99x10^{-3}$	$8.77x10^{-2}$	
.0620	$1.9x10^{-2}$	$7.06x10^{-2}$	
.049	$1.9x10^{-2}$	$9.42x10^{-2}$	
.0287	$1.9x10^{-2}$	$1.04x10^{-1}$	
.0217	$1.9x10^{-2}$	$1.12x10^{-1}$	
.0196	$1.9x10^{-2}$	$1.35x10^{-1}$	
.0190	$1.9x10^{-2}$	$1.02x10^{-1}$	
.0170	$1.9x10^{-2}$	$1.47x10^{-1}$	
.0140	$1.9x10^{-2}$	$1.55x10^{-1}$	
.007	$1.9x10^{-2}$	$2.47x10^{-1}$	

45.0°C

$HClO_4$ Solution

7.79 M	$3.3x10^{-2}$ M	$5.39x10^{-1}$	$7.62x10^{-2}$
5.63	$3.3x10^{-2}$	$3.32x10^{-1}$	$6.33x10^{-2}$
4.68	$3.3x10^{-2}$	$2.66x10^{-1}$	$8.50x10^{-2}$
3.29	$3.3x10^{-2}$	$19.x10^{-1}$	$7.63x10^{-2}$
2.33	$3.3x10^{-2}$	$2.07x10^{-1}$	$6.40x10^{-2}$
1.06	$3.3x10^{-2}$	$1.00x10^{-1}$	
0.61	$3.3x10^{-2}$	$1.40x10^{-1}$	

$LiClO_4$ (μ = 2.00)

2.05 M	.42 M	$1.21x10^{-1}$
0.91	.21	$9.37x10^{-2}$
0.408	.10	$1.01x10^{-1}$
0.307	$6.7x10^{-3}$	$1.44x10^{-1}$
0.25	$4.2x10^{-2}$	$1.14x10^{-1}$

45.0°C

$LiClO_4$ (μ = 2.00)

$[H^+]$	$[Cr^{3+}]$	$k_{obs}(min^{-1})$ (1st step)	$k_{obs}(hr^{-1})$ (2nd step)
0.267 M	$3.7x10^{-2}$ M	$1.27x10^{-1}$	
0.187	$6.7x10^{-3}$	$1.25x10^{-1}$	
0.0878	$6.7x10^{-3}$	$1.94x10^{-1}$	
0.086	$1.2x10^{-3}$	$1.37x10^{-1}$	
0.070	$9.0x10^{-3}$	$1.49x10^{-1}$	
0.0692	$3.8x10^{-3}$	$1.83x10^{-1}$	
0.043	$6.0x10^{-3}$	$1.70x10^{-1}$	
0.0347	$1.9x10^{-3}$	$2.05x10^{-1}$	
0.0287	$3.0x10^{-3}$	$2.10x10^{-1}$	
0.0285	$1.31x10^{-3}$	$1.98x10^{-1}$	
0.025	$3.0x10^{-3}$	$2.09x10^{-1}$	
0.0132	$1.7x10^{-3}$	$3.36x10^{-1}$	
0.011	$1.5x10^{-3}$	$4.67x10^{-1}$	
0.010	$1.6x10^{-3}$	$2.84x10^{-1}$	
0.009	$1.5x10^{-3}$	$3.55x10^{-1}$	
0.006	$1.2x10^{-3}$	$4.57x10^{-1}$	
0.0057	$1.2x10^{-3}$	$6.83x10^{-1}$	
0.0047	$1.1x10^{-3}$	$8.13x10^{-1}$	
0.0046	$1.0x10^{-3}$	$6.48x10^{-1}$	

$NaClO_4$ (μ = 2.00)

0.762M	$6.1x10^{-2}$M	$1.12x10^{-1}$	
0.346	$3.12x10^{-2}$	$1.42x10^{-1}$	
0.330	$2.2x10^{-2}$	$1.17x10^{-1}$	
0.216	$2.2x10^{-2}$	$1.43x10^{-1}$	
0.197	$2.2x10^{-2}$	$1.63x10^{-1}$	
0.141	$1.04x10^{-2}$	$1.68x10^{-1}$	
0.088	$5.7x10^{-3}$	$2.25x10^{-1}$	
0.082	$2.4x10^{-2}$	$1.90x10^{-1}$	

45.0°C

$NaClO_4$ (μ = 2.00)

$[H^+]$	$[Cr^{3+}]$	$k_{obs}(min^{-1})$ (1st step)	$k_{obs}(hr^{-1})$ (2nd step)
.071 M	2.4×10^{-2} M	1.97×10^{-1}	
.056	2.4×10^{-2}	2.55×10^{-1}	
.030	2.4×10^{-2}	2.75×10^{-1}	
.029	2.4×10^{-2}	2.18×10^{-1}	
.022	2.4×10^{-2}	2.66×10^{-1}	
.017	2.4×10^{-2}	2.92×10^{-1}	
.016	2.4×10^{-2}	4.20×10^{-1}	
.015	2.4×10^{-2}	3.28×10^{-1}	
.012	2.4×10^{-2}	3.99×10^{-1}	
.011	2.4×10^{-2}	55.1×10^{-1}	

The change in rate constant in regions of low acidity (below 0.1M) cannot be explained by a salt effect since the magnitude of the change is so large. The effect can be accounted for if the following reactions are assumed to be taking place:

$$CrOHCr^{5+} + H_2O \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} Cr_2(OH)_2^{4+} + H^+ (Q_{21} = k_{-1}/k_1) \qquad \text{(V-23)}$$

$$CrOHCr^{5+} + H_2O \overset{K_{hyd}}{=} CrOHCrOH^{4+} + H^+ \qquad \text{(V-24)}$$

$$CrOHCrOH^{4+} \underset{k'_1}{\overset{k'_{-1}}{\rightleftharpoons}} Cr_2(OH)_2^{4+} . \qquad \text{(V-25)}$$

Then

$$-\frac{d[CrOHCr^{5+}]}{dt} - \frac{d[CrOHCrOH^{4+}]}{dt} = k_{-1} [CrOHCr^{5+}] + k'_{-1} [CrOHCrOH^{4+}]$$
$$-k_1 [Cr_2(OH)_2^{4+}][H^+] - k'_1 [Cr_2(OH)_2^{4+}]. \qquad \text{(V-26a)}$$

Substituting K_{hyd} $[CrOHCr^{5+}][H+]$ for $[CrOHCrOH^{4+}]$, Eq. (V-26a) can be rewritten as

$$-\frac{d[CrOHCr^{5+}]}{dt} (1 + K_{hyd}/[H+]) = [CrOHCr^{5+}](k_{-1} + k'_{-1} K_{hyd}/[H+])$$
$$-[Cr_2(OH)_2^{4+}] \{k_1[H^+] + k'_1\}. \qquad \text{(V-26b)}$$

But at equilibrium

$$Q_{21} = \frac{[Cr_2(OH)_2^{4+}][H^+]}{[CrOHCr^{5+}]} = k_{-1}/k_1 = k'_{-1}/k'_1 K_{hyd} \qquad \text{(V-27)}$$

and therefore

$$-\frac{d[CrOHCr^{5+}]}{dt} \{1 + K_{hyd}/[H^+]\} = [CrOHCr^{5+}]\{k_{-1} + k'_{-1} K_{hyd}/[H^+]\}$$
$$-[Cr_2(OH)_2^{4+}]\{k_{-1}[H^+]/Q_{21} + k'_{-1} K_{hyd}/Q_{21}\}$$
$$= [CrOHCr^{5+}]\{k_{-1} + k'_{-1} K_{hyd}/[H^+]\} - \{\Sigma-[CrOHCr^{5+}](1+K_{hyd}/[H^+]\}$$
$$+ \{k_{-1}[H^+]/Q_{21} + k'_{-1} K_{hyd}/Q_{21}\} \qquad \text{(V-26c)}$$

and the apparent first order rate constant can be calculated by standard procedures as:

$$\frac{k_{-1} + k'_{-1}\, K_{hyd}/[H^+] + (1 + K_{hyd}/[H^+])\{k_{-1}[H^+]/Q_{21} + k'_{-1}\, K_{hyd}/Q_{21}\}}{1 + K_{hyd}/[H^+]} = k_{obs} \quad \text{(V-28)}$$

In regions of low acidity, the back reaction term:

$$1/Q_{21}(1+K_{hyd}/[H^+])\{k'_{-1}\, K_{hyd} + k_{-1}\, [H^+]\} \quad \text{(V-29)}$$

becomes negligible and:

$$k_{obs} \simeq \frac{k_{-1} + k'_{-1}\, K_{hyd}/[H^+]}{1 + K_{hyd}/[H^+]} \quad . \quad \text{(V-30)}$$

By estimating k_{-1} from the minima in the plots of log k_{obs} versus the log of the hydrogen ion concentration and using the observed rate data for a given hydrogen ion concentration, it is easy to solve a pair of simultaneous equations and find values for k_{-1} and K_{hyd}. With these computed values and using rate data at higher acidities within the same range of ionic strength, a value for Q_{21} can be obtained. Then the full expression for the observed rate given in Eq. (V-28) can be evaluated at acid concentrations throughout the range studied and curves drawn through the plotted points should reproduce the observed data. In Fig. 8, the theoretical curves for each set of data are shown as the lines drawn through the scattered observed points.

Table VI gives the values calculated for Q_{21}, k_{-1}, k'_{-1}, and K_{hyd}. The values for Q_{21} obtained by this method can be compared with the values for the same quantity calculated from the optical density of the acid solutions when the first stage of the reaction is complete. The percent of each complex can be found from the known absorbancies of the two

Table VI. Values of Parameters Calculated from Rate Data and Equation (V-30) (μ = 2.00)

T(°C)	Q_{21}	k_{-1}	k'_{-1}	K_{hyd}
25.0	1.24	0.0070	0.0487	0.0235
35.5	1.76	0.0210	0.255	0.0188
45.0	2.54	0.0600	0.513	0.0300

complexes: at 2700 Å, the absorbance of the intermediate is 13.1 and that of the blue species is 28.5. Since the hydrogen ion concentration has been determined, Q_{21} can be calculated, yielding values of 2.20, 2.78, and 3.06 at 25.0°C, 35.5°C, and 45.0°C. The values obtained in this manner are somewhat higher than those reported above at μ = 2.00 but no attempt was made to maintain constant ionic strength in these solutions and the considerable variation of the activities of the reacting species may well account for the variation.

A plot of Q_{21} versus 1/T yields a value of 6.8 kcal/mole for ΔH of reaction (V-23) and the value of $\Delta S_{298°}$ calculated from these data is 23 e.u. The observed positive entropy change can be correlated with the production of two charged species.

At first blush the calculated hydrolysis constant seems to be quite high. However, comparison with some data on analogous ammine complexes of chromium (III) lends support to the calculated K_{hyd} for the aquo complex of chromium (III). Wilmarth, Graff, and Gustin[29] measured the acidity constants of aquopentamminechromium (III), diaquotetramminechromium (III), decammine-μ-hydroxodichromium (III), and aquononammine-μ-hydroxodichromium (III) ions and reported pK's of 5.2, 5.5, 7.8, and 2.8 respectively for

the individual species. The pK of hexaquochromium (III) is reported as 3.82 by Postmus and King.[22] The difference between the pK values of the latter and aquopentamminechromium (III) represents a 24-fold difference in acidity, the aquo complex being the more acidic. Similar correlation is observed between the calculated hydrolysis constant of the intermediate, decaquo-μ-hydroxodichromium (III), and the aquononammine-μ-hydroxodichromium (III) complex: the pK's are 1.6 and 2.8 respectively and represent a 15-fold difference in acidity, the aquo complex again being more acidic than the ammine.

There are at least three other known di-hydroxo bridged chromium (III) complexes: tetraphenanthroline-μ-dihydroxodichromium (III), tetraethylenediammine-μ-dihydroxodichromium (III), and tetraoxalato-μ-dihydroxodichromate (III). Both strong and weak field ligands are represented since the organic ligands produce strong fields and the oxalate ligand, like water, is a weak-field ligand.

Kinetic studies by Grant and Hamm[8] have been carried out using the oxalato complex, and comparison with these results should be of interest since the two ligands produce ligand fields of comparable strength. The over-all reaction scheme for the two systems is the same: a two-step decomposition of the dimer to monomeric chromium (III) complexes by way of a single-bridged intermediate. Since conductometric measurements were used to follow the reaction of the oxalato complex with perchloric acid, no attempt was made to maintain ionic strength.

Grant and Hamm observed a two-step process in the acid decomposition of tetraoxalato-μ-dihydroxodichromate (III) complex. They postulate the breaking of a single hydroxo bridge as the rate determining step in the first process. The second slow step is assumed to proceed by two paths:

in sufficient acid, the breakdown is first order in chromium, and in deficient acid, a more rapid parallel step presumably goes by way of an acid-dissociation product of the singly-bridged hydroxo intermediate and is pseudo-first order in chromium.

Unfortunately no comparison of $\Delta F^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the first step can be made since the rate laws are different. More interesting and fruitful comparison would be possible if rate data were available for the other dihydroxo bridged complexes since all represent neutral ligands in the remaining octahedral positions, and of course if the rate law includes hydrogen ion dependence.

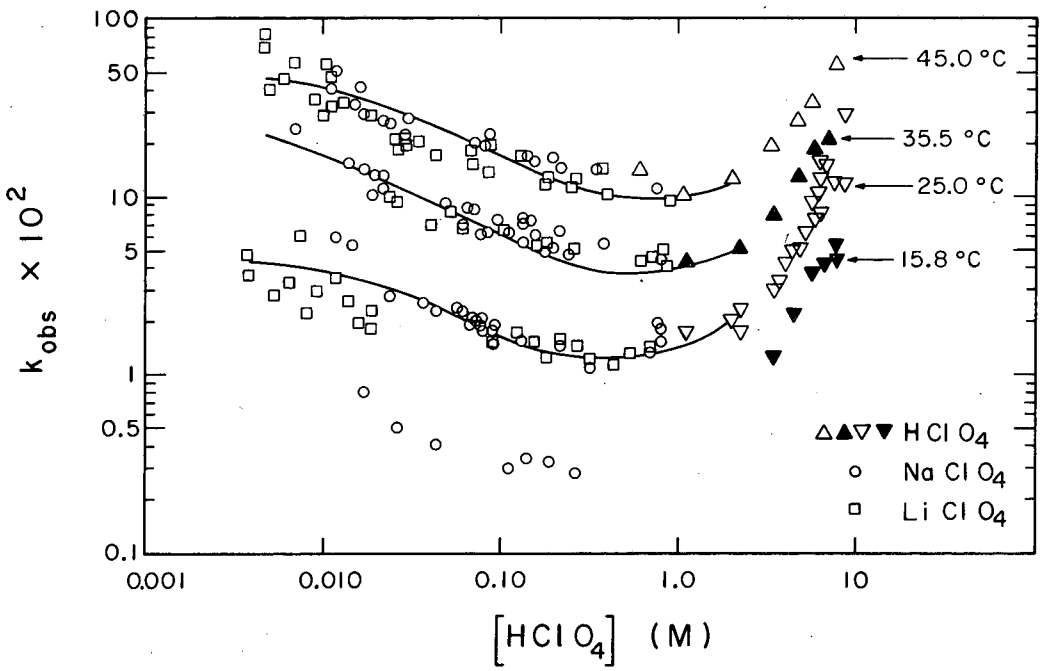
In sufficient acid the second step of the oxalato reaction is hydrogen ion independent, and here $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be compared. Grant and Hamm report values of 13.4 kcal/mole for $\Delta H^{\ddagger}$ and -36 ± 2 e.u. for $\Delta S^{\ddagger}$ when the reactions take place in sufficient acid. The condition of "sufficient acid" is surely fulfilled in the reactions being studied here.

Table VII gives the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values calculated for both steps of the acid decomposition of the dimer $Cr_2(OH)_2^{4+}$ and for the formation of the dimer from the intermediate. In the second step of the decomposition of the dimer a value of 17.0 ± 1.0 kcal/mole for $\Delta H^{\ddagger}$ and -18 ± 4 e.u. for $\Delta S^{\ddagger}$ have been calculated here for a 3.3 M $HClO_4$ solution.

It is interesting to note that $\Delta S^{\ddagger}$ for the reaction of $CrOHCr^{5+}$ to give monomers involves in the rate determinations step the displacement of an hydroxide group by a water molecule. Powell[30] suggested at one time that the binding of a water molecule in the activated complex should show a small entropy change of ~ 3 e.u. It is evident that for complexes like these, this is an over simplified approach and perhaps greater weight should be attributed to the loss of translational freedom.

Table VII $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ Calculated for Acid Decomposition of Dimeric Species

$[H^+]$ (M)	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (cal/mole-°)
	dimer → intermediate	
7.7	13.7	-24.3
6.6	14.3	-23.7
5.6	13.4	-25.6
4.4	14.1	-27.3
3.3	15.7	-23.7
2.2	14.8	-26.6
1.1	13.5	-29.6
	intermediate → dimer	
0.200	21.0	- 4.5
0.188	21.4	- 3.8
0.082	21.4	- 4.3
0.022	21.1	- 3.3
	intermediate → monomer	
6.6	15.5	-29
5.6	15.5	-29
4.4	16.6	-23
3.3	17.0	-18



MU-34078

Fig. 8

3. Attempts to Isolate the Intermediate

The existence of a new chromium (III) polymer in acid solutions may be postulated from the observed behavior of the dimer under these conditions. As the acid concentration of the reaction mixture of dimer and perchloric acid was raised, the solution became progressively more green in color, indicating the increasing concentration of the new species. When fresh dimer was injected into concentrated perchloric acid, the now light green solution gave a reproducible spectrum throughout the 10.5 to 12.0M perchloric acid concentration range each time the material was prepared. The spectrum of the resulting solution is shown in Fig. 1 and the absorbances at the maxima are 16.4 at 590 mμ and 20.7 at 424 mμ. Comparison of the spectra of dimer and intermediate shows a shift to higher wavelength of both maxima but the absorbance per mole of Cr is about the same.

Attempts to isolate the new species on ion-exchange columns proved uniformly unsuccessful. When the intermediate, formed in concentrated perchloric acid, was put on an ion-exchange column, the resin disintegrated. In solutions of lower perchloric acid concentration - ca. 8M - sufficient quantities of the new species were calculated to be present on the basis of the optical density of the solution at the end of the first step and the known chromium (III) concentration, to warrant attempts at separation. When solutions of this concentration in acid were applied to a column of resin, two bands were observed: a blue band associated with the known dimeric species and a green band, nearly three-fourths the amount of the blue and absorbed in a higher position relative to the blue band on the column. Attempts to move the new species from the column did not prove successful since within the time required to move it from the column reaction with the aqueous eluant reversed the equilibrium between the two species and produced only the blue dimer. Cold columns were used in an attempt to

slow down the reverse reaction, but none of the material could be obtained from the column since it could not be displaced before it reverted to the blue species - even using thorium perchlorate in 1.0M acid as an eluant.

The evidence from these experiments indicates only that a new species has been formed during the reaction of the dimer with acid, that the new species is of higher charge than the dimer, that it can be easily converted to the blue dimer in aqueous solution, and that it is of the same degree of polymerization since the dependence on chromium is the same in the rate law. Further characterization of the material will be made in later sections.

4. Formation of the Dimer by Oxidation of Chromium (II) Solutions

One possible path for the known formation of the dimer in the oxidation of Cr(II) solutions by molecular oxygen may be through the intermediate discovered in the course of this work. It was noted that when oxygen was introduced into Cr(II) solutions, the color change observed within the first few seconds was from the clear sky-blue of the Cr(II) ion to an intense green color. Since the spectrum of the intermediate, also green in color, is known, it was thought that following the spectrum of the oxidized solution with time might show the formation of the intermediate. Accordingly samples from the Cr(II) solutions in the process of being oxidized were removed at intervals of 7.5, 15, 30, 45, 60 and 90 seconds after the introduction of oxygen; two samples were diluted to a volume of 100 cc in volumetric flasks, one with distilled water and the other with a 2M solution of lithium perchlorate and the change in the spectrum followed with time. The spectrum of the initially formed material is constant from the first to the last of the withdrawn samples but is not that of the dimer or the intermediate (see Fig. 1). However, the final spectrum of the diluted samples shows the presence of the dimer after a period of about

one hour since the spectrum is essentially that of the dimer. These runs were carried out at 25°C, the solutions, cell compartment and cell holder being thermostatted at that temperature. Similar runs at 45°C gave like results, although the spectra passed through an absorption maximum corresponding to the dimer and then began to decay, reflecting decay to the monomeric species. Chromium (III) concentrations were of the order of 4.1×10^{-3} M and the acid concentration 3.3×10^{-3} M.

Using the same sampling techniques, the change in absorbance at 2700 Å was also followed using solutions made up in the same way: one in which the ionic strength was maintained at 2.00 with lithium perchlorate, and one with distilled water only. No difference in the rate of formation of the dimer was observed, either as a function of ionic strength or length of time in which the oxidative process was allowed to proceed, after the first 30 seconds. Table VIII gives the observed first order rate constants at 25°C.

Table VIII. Observed Rate Constants at 25.0°C for Formation of Dimer in O_2-oxidized Cr(II) Solutions

$[H^+]$ (M)	t(sec) of oxid	k_{obs} $\mu = 2.00$	variable μ
4.3×10^{-3}	7.5	5.12×10^{-2} min^{-1}	6.13×10^{-2} min^{-1}
3.55×10^{-3}	15	2.47×10^{-2}	3.74×10^{-2}
3.30×10^{-3}	30	3.49×10^{-2}	2.71×10^{-2}
3.12×10^{-3}	45	3.43×10^{-2}	3.76×10^{-2}
9.8×10^{-3}	60	3.12×10^{-2}	3.12×10^{-2}
1.00×10^{-2}	90	3.73×10^{-2}	2.83×10^{-2}

Conceivably the initial product or products may include the intermediate and some higher polymer of chromium. Both Ardon and Plane[19]

and Joyner and Wilmarth[31] have suggested the formation of peroxo-bridged complexes in the oxidation of Cr(II) in acidic and ammoniacal solutions to form dimeric chromium (III) compounds. The following scheme can be advanced to explain the formation of some intermediate and higher polymers:

$$O_2 + Cr^{2+} = Cr:\ddot{O}:\ddot{O}:^{+2} \qquad \text{(V-31)}$$

$$CrOO^{2+} + Cr^{2+} = Cr:\ddot{O}:\ddot{O}:Cr^{4+} \qquad \text{(V-32)}$$

$$CrOOCr^{4+} + Cr^{2+} = Cr:\ddot{O}:Cr^{4+} + Cr\text{-}O^{2+} \qquad \text{(V-33)}$$

$$CrO^{2+} + Cr^{2+} = Cr:\ddot{O}:Cr^{4+} \qquad \text{(V-34)}$$

$$CrOCr^{4+} + H^{+} = CrOHCr^{5+} \qquad \text{(V-35)}$$

$$CrOOCr^{4+} + Cr^{2+} = Cr:\ddot{O}:\ddot{O}:Cr:\ddot{O}:Cr^{6+} \qquad \text{(V-36)}$$

$$Cr^{2+} + CrOOCrOCr^{6+} = CrOCrOOCrOCr^{8+} \qquad \text{(V-37)}$$

$$CrOCrO\text{-}O\text{-}CrOCr^{8+} = 2CrOCrO^{4+} \qquad \text{(V-38)}$$

$$CrOHCr^{5+} = Cr_2(OH)_2^{4+} + H^{+} \qquad \text{(V-39)}$$

A simple method can be devised to test the hypothesis of higher polymer formation using viscosity measurements of the oxidation products and the three known species, monomer, dimer, and trimer, at 4°C. It would be preferable to use the electrolytic method of Ardon and Plane[19] to prepare the original Cr(II) solutions since no correction for the presence of zinc perchlorate would then have to be included.

Plane and Kolaczkowski[20] have attempted to show that the oxidation of Cr(II) by molecular oxygen is second order in chromium (II) but directly proportional to the flow of oxygen gas. The results of their experiments seem to indicate that the reaction is in fact diffusion-controlled - an observation supported by earlier work on Cr(II) solutions carried out by Stone.[32] Stone reports that the rate of reaction of dissolved oxygen is so rapid that the rate of dissolution by bubbling can be neglected. In fact, Cr(II) solutions react more rapidly with molecular oxygen (and

hydrogen peroxide) than other common oxidizing agents. He suggests the Cr(II) reactions are more rapid because of a strong coordinating tendency to form stable hydroxy or oxy-bridge complexes. Ardon and Plane[19] pointed out that two-electron oxidants gave mainly the dimer product while oxidation with one-electron oxidants like Fe(III) and Cu(II) gave monomeric Cr(III). Thus the evidence points to a peroxo-bridge complex of Cr(IV) as an intermediate. Since the product first formed is not the dimer, the simple scheme suggested by Plane and Kolaszkowski seems suspect. The process is a most complex one and further investigation of it is called for, perhaps through an elucidation of the products formed by such techniques as molecular weight determinations and freezing point lowering.

C. Characterization of Polymeric Species

1. Determination of Degree of Polymerization by Freezing Point Depression Measurements

Fresh samples of the blue species, 0.370 and 0.571 M in chromium (III), were prepared by displacement from ion-exchange columns and small portions added by means of micropipetes to 10.00 cc of chilled 41.7% perchloric acid (13.0106 g). The solutions were stirred vigorously and the cooling curve followed with time. After freezing, the solutions were allowed to warm to room temperature and after 30 minutes were cooled again to the freezing point.

Fresh samples of the green polynuclear species, 0.743 and 0.809M, were prepared from refluxed chromium (III) perchlorate solutions by displacement from a column of Dowex 50W-X4 exchanger and small portions added to 10.00 cc of chilled 41.7% perchloric acid by means of a micropipete.

Table IX gives the freezing point depression obtained with each of the polynuclear species. The first column gives the chromium (III) concentration in moles per kilogram of perchloric acid (40.7%).

Table IX Cryoscopy of Polynuclear Chromium Species

Moles added per 1000 g eutectic mixture	ΔT	$\Delta T/m = K_f$
	Blue Species	
.00711	0.0165°	2.31°
.01136 [a]	0.0278°	2.44° *
.01309	0.0284°	2.17°
.01421 [a]	0.0298°	2.10° *
.0305	0.0659°	2.16°
.0685 [a]	0.153°	2.24° *
	Intermediate	
.01136 [a]	0.0278°	2.44° *
.01421 [a]	0.0298°	2.10° *
.0685 [a]	0.153°	2.24° *
	Green Species	
.00616	.0090°	1.46°
.0124	.0184°	1.48°
.0284	.0423°	1.49°
.0455	.0670°	1.47°

[a] Solutions allowed to warm room temperature and rechilled

* Same value observed for chilled solutions, and warmed and rechilled solutions

Since

$$\Delta T/m = 1/n \cdot K_f \qquad \text{(V-40)}$$

where n is the number of chromium atoms per complex ion, it can be seen that both the blue species and the intermediate are dimeric in character, since the K_f observed is 2.21° and that reported for the perchloric acid-water eutectic is 4.43°. The green species has also been shown to be trimeric since the observed K_f is one-third the reported value.

2. Measurement of Variation of Magnetic Susceptibility with Temperature

The susceptibility of each sample was calculated using the following relations:

$$10^6\ \chi_{Cr}(\text{c.g.s.}) = \beta(F_{sample} - F_{solvent}) - 10^6 \chi_{solvent}(w_{solvent\ in\ sample} - w_{solvent}) \qquad \text{(V-41)}$$

and

$$\chi_A = \frac{\chi\ \bar{C}r}{\text{gram atoms of Cr in sample}} \qquad \text{(V-42)}$$

where F is in milligrams, β the tube constant.

Correction for the diamagnetism of the individual ions was made by using the following values: OH^-, 12.0; Cr^{3+}, 13; H_2O, 13; and ClO_4^-, 32 (all multiplied by -1×10^{-6});[38] the susceptibility of perchloric acid was found to be -0.418×10^{-6}, at 20°C.

a. Theoretical Treatment of Data -

(1) Dimeric Species

Binuclear complexes contain two atoms each of which possesses a spin angular momentum, and it is certainly possible and indeed likely that these two atoms will interact. Following the general procedure of Kambe[34] such an interaction can be treated as a spin-spin coupling of the form

$$\mathcal{H} = -2J\, \underset{\sim}{S}_1 \cdot \underset{\sim}{S}_2 \qquad \text{(V-43)}$$

where J is the exchange coupling constant and $\underset{\sim}{S}_1$ and $\underset{\sim}{S}_2$ are the spin vectors of the two atoms. Since $\underset{\sim}{S}_1$ and $\underset{\sim}{S}_2$ have the same magnitude, the Hamiltonian can be reduced to:

$$\mathcal{H} = -J\, \{S'(S' + 1) - 2S(S + 1)\} \qquad \text{(V-44)}$$

where S is the eigenvalue of the spin vectors of each atom (3/2 for the present case), S' = 2S, 2S - 1,...,0 and therefore here S' = 3,2,1,0. Taking J to be negative, the energy level scheme will then be given by:

$$E = -J\, \{S'(S' + 1) - 2S(S + 1)\} \qquad \text{(V-45)}$$

each level being 2S' + 1 degenerate. Therefore there is a low-lying singlet and a triplet at a distance of 2J above it.

The blue species has been shown to be dimeric, and to have two bridging hydroxy groups.[20] The intermediate, a dimeric species assumed to be formed by a single bridging hydroxy group, will have the same Hamiltonian as the blue dimer and the same theoretical derivation for the variation of χ_A with temperature. The variation of the atomic susceptibility, χ_A, with temperature is given for S = 3/2,3/2 - the case for spin-free chromium (III) - by the expression:

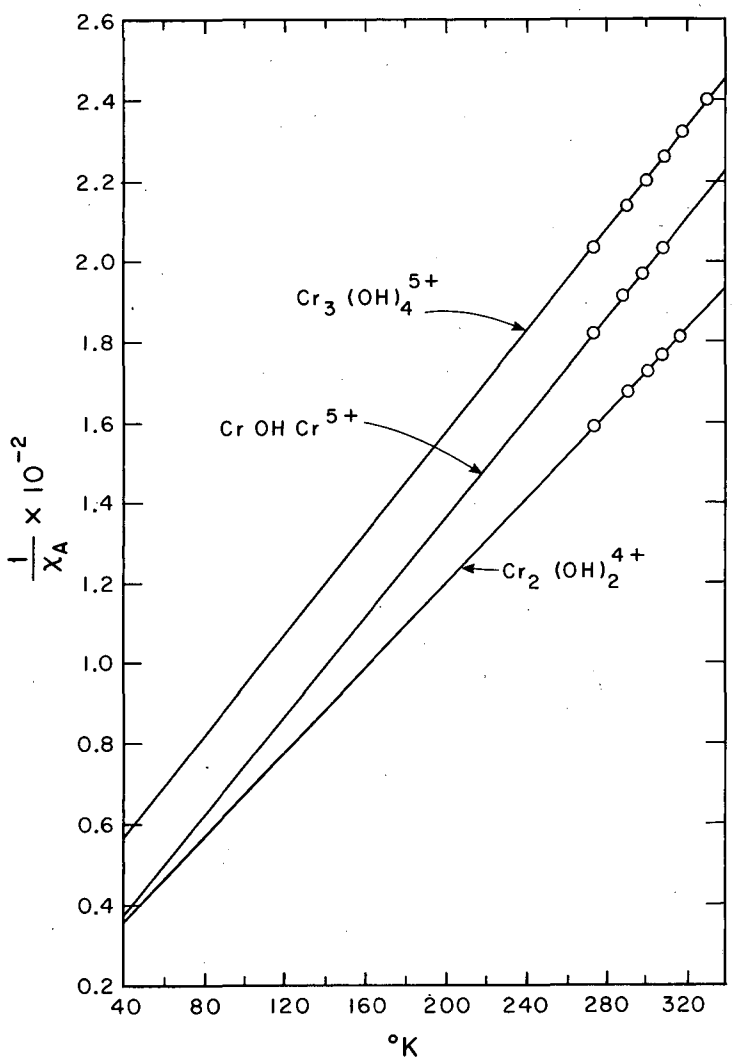
$$\chi_A = \frac{g^2 N\beta^2}{3kT} \left\{ \frac{42 + 15\exp(6x) + 3\exp(10x)}{7 + 5\exp(6x) + 3\exp(10x) + \exp(12x)} \right\} + N(\alpha) \qquad \text{(V-46)}$$

following Kambe's general procedure, where x = -J/kT, g is the spectroscopic splitting factor, β the Bohr magneton, k the Boltzmann constant, T the absolute temperature, and N(α) the temperature-independent, high-field paramagnetic term. The presence of such an interaction, J, is related to an observed and finite value of θ in the Curie-Weiss equation, $\chi = C/(T + \theta)$. There may be other explanations of course for an appreciable value of θ.

When the value of T, in degrees Kelvin, approaches the value of J, significant magnetic deviation occurs. Throughout the temperature range covered in this experiment, however, T is much greater than J, and no such deviation is observed.

Table X gives the value of J, g, μ_{eff} (the effective magnetic moment) at 20°C, $N(\alpha)$, and Θ observed for the blue dimer and intermediate species. The g values were obtained by an independent ESR measurement. These values can be compared with those reported by Earnshaw and Lewis[26] for similar species, and with the values reported by Mulay and Naylor[35] for monomer and blue dimer. Table XI gives the experimental data from which χ_A for each species was calculated. A plot of χ_A versus 1/T is given in Fig. 9 for both dimeric species. Only a small temperature range was covered in these measurements since no crystals of either material have been obtained and the measurements must therefore be made on solutions. It may be possible to go to lower temperatures for the solutions in perchloric acid - measurements made on the intermediate - since the freezing point of perchloric acid of comparable acidity is about -30°C. The higher temperatures cannot be used since both the blue dimer and the intermediate decompose to form the monomer, actually precipitating in the latter instance as fine crystals in the perchloric acid medium. It should be noted that measurements of magnetic susceptibility of solutions tend to be slightly higher in value than those measured on single crystals of the same substance.[36]

It may have been anticipated that only a small coupling of spins- indicated by the low value of J - would be observed in these species since the spectra of the two species (see Fig. 1) do not differ drastically from the hexaquochromium (III) spectrum, as indicated by Schaffer's and Jorgensen's empirical correlation of spectral and magnetic data on chromium (III) ammine



MU-34079

Fig. 9

Table X. Reported Values of Susceptibility Parameters for Chromium (III) Complexes

Complex	μ_{eff} (B.M.)	J	g	$N(\alpha)x10^6$	θ	Ref
$[(phen)_2Cr(OH)_2(phen)_2]^{4+}$	3.67	10	1.99	58	35°	26
$[(gly)_2^2 Cr(OH)_2Cr(gly)_2]^{4+}$	3.80	6	2.01	52	20°	26
$[(phal)_2Cr(OH)_2Cr(phal)_2]^{4+}$	3.84	7	2.03	44	30°	26
$(aq)_4Cr(OH)_2Cr(aq)_4^{4+}$	3.74	7.5	1.98	58	27°	This work
$(NH_3)_5CrOH(NH_3)_5^{5+}Br_5$	3.44	20.25	1.94	62	120°	26
$(NH_3)_5CrOH(NH_3)_4(H_2O)^{5+}Br_5$	3.52	20.7	1.99	56	130°	26
$(NH_3)_5CrOH(NH_3)_4(H_2O)^{5+}Cl_5$	3.62	20.7	1.99	56	130°	26
$(NH_3)_5CrOCr(NH_3)_5Br_5$	3.50	14	1.91	56	70°	26
$[(aq)_5CrOHCr(aq)_5]^{5+}$	3.48	16	1.92	52	22°	This work
$Cr(aq)_6(ClO_4)_3$	3.87					35
	3.89					This work

phen = phenanthroline

gly = glycine

phal = phenylalanine

aq = water

Table XI. Experimental Data for Calculations of χ_A & μ_{eff}

T(°C)	F_{sample}	$F_{solvent}$	$\bar{\chi}_{er}$	$\chi^{(a)}$	$\chi_{\mu}^{(b)}$	χ'_{μ}	χ_A	$\mu_{eff}^{(c)}$ (B.M.)	(B.M.)
				Room Temperature					
				Monomer					
293.2	41.21	-56.77	20.690	13.584	6,228	6,402	6,402	3.89	3.89
				Dimer					
293.2	52.61	-50.95	22.248	17.117	11,640	11,826	5,913	3.74	
				Trimer					
293.2	71.15	-50.90	19.923	15.006	13,528	13,905	4,635	3.310	
				Variation with Temperature					
				Dimer					
274.0	36.43	-35.21	24.176	18.252	12,411	12,597	6,299	3.73	
290.2	35.69	-35.24	22.903	17.291	11,758	11,944	5,972	3.74	
294.6	33.63	-35.18	22.210	16.768	11,402	11,588	5,794	3.74	
307.7	32.04	-35.18	21.690	16.375	11,135	11,321	5,660	3.75	
316.9	30.31	-35.19	21.127	15.950	10,846	11,032	5,516	3.75	
				Intermediate					
274.0	41.67	-35.18	24.582	13.533	10,806	10,969	5,485	3.48	
287.9	37.90	-35.15	23.348	12.853	10,263	10,427	5,213	3.48	
298.5	36.06	-35.09	22.726	12.511	9,990	10,154	5,077	3.50	
308.1	33.88	-35.03	21.993	12.107	9,668	9,831	4,916	3.50	

Table XI. Experimental Data for Calculations of χ_A and μ_{eff} (continued)

T(°C)	F_{sample}	$F_{solvent}$	$\bar{\chi}_{er}$	$\chi^{(a)}$	$\chi_\mu^{(b)}$	χ'_μ	χ_A	$\mu_{eff}^{(c)}$ (B.M.)
				Trimer				
274.0	90.58	-35.21	40.523	15.954	14,382	14,759	4,920	3.29
290.2	84.39	-35.24	38.508	15.160	13,667	14,044	4,681	3.30
300.0	80.86	-35.18	37.334	14.698	13,251	13,628	4,543	3.30
308.7	78.11	-35.18	36.338	14.306	12,897	13,274	4,425	3.31
318.4	74.82	-35.19	35.362	13.921	12,550	12,927	4,309	3.31
329.9	70.92	-35.18	34.083	13.418	12,097	12,474	4,158	3.30

a $\chi = \bar{\chi}_{Cr}/W$, and W = weight of sample x % chromium in sample on a weight/weight basis.

b $\chi_\mu = \chi$ x M.W. of complex

c $\mu_{eff} = 2.839 \sqrt{\chi_A T}$

dimers.[37]

The complex octaquo-μ-dihydroxodiiron(III) has been deduced to be diamagnetic by Mulay and Selwood[38] while the analagous chromium(III) complex reported here is found to be paramagnetic to the extent of three unpaired electrons per chromium. In fact all of the $Cr_2(OH)_2^{4+}$ complexes studied by Earnshaw and Lewis[26] show a similar behavior, even with strong field ligands occupying the remaining octahedral positions.

Some coupling of the spins in the chromium (III) complexes can be deduced from the small value of J observed but this result should be compared with the J value of 490°, reported by Elliott,[38] for tetraphenanthroline-μ-dihydroxodiiron(III) with an effective magnetic moment of 1.6 B.M. corresponding to one unpaired electron per iron. The analagous chromium (III) complex, tetraphenathroline-μ-dihydroxodichromium (III), as reported by Earnshaw and Lewis, has a J value of 10° and an effective magnetic moment of 3.83 B.M., equivalent to three unpaired electrons per chromium.

Any argument for the difference in behavior of the two transition elements must be related to the number of d electrons available. Fe(III) has five d electrons; in a weak octahedral field there would be expected to occupy singly both the t_{2g} and e_g orbitals (a spin-free complex) while in a strong field only the t_{2g} orbitals will be occupied (a spin-paired complex). Each bridging hydroxy group has a pair of electrons to contribute to π bonding in addition to the two pair used in σ bonding to the metal atoms and the σ bond to the hydrogen. If sp^2 hybridization is postulated, then a p_z orbital, perpendicular to the plane of the bridging groups and metal atoms, becomes available to allow for spin-spin coupling through the d_{xz} and d_{yz} orbitals of appropriate symmetry. Since each hydroxy group contributes two electrons to π bonding orbitals, a total of fourteen and ten

electrons, respectively, for the iron and chromium doubly bridged dimers must be accomodated.

In such dimeric complexes each individual metal atom has a crystal field of C_{2v} symmetry (see Fig. 10a). Under this symmetry the s, p, and d orbitals will have symmetry $4A_1 + A_2 + 2B_1 + 2B_2$ and the ligands $4A_1 + B_1 + B_2$. For each complex, there are twelve σ bonds from the central metal atom to eight waters and two hydroxy ligands. There then remain the non-bonding orbitals, d_{xy}, d_{xz}, and d_{yz}, of symmetry $A_2 + B_1 + B_2$. Assuming the $M\langle^{OH}_{OH}\rangle M$ group to be planar, the complex as a whole has D_{2h} symmetry. The choice of $C_2(x)$ and $C_2(y)$ axes is arbitrary in D_{2h}, but, given a selection, the orbitals A_u, B_{1g}, B_{2g}, B_{1u}, B_{2u}, and B_{3g} can be formed from the non-bonding orbitals of the two metal atoms. Since the two atoms are rather far from one another - ca. 2.8Å using ionic radii - the orbitals would be expected to be nearly degenerate pair by pair. Using the interaction with the π orbitals of the bridging hydroxy groups transforming as $B_{3g} + B_{2g} + 2B_{1u}$ ($\chi_\pi(\perp)$) results in the following energy scheme:

$$(B^b_{3g})(B^b_{2g})(B^b_{1u})(A_u)(B_{1g})(B_{2u})(B^*_{3g})(B^*_{2g})(B^*_{1u}). \qquad \text{(V-47)}$$

The absolute order of the levels is unknown, but the degeneracy has been split by π bonding.

With fourteen electrons, the electronic configuration should be:

$$(B^b_{3g})^2(B^b_{2g})^2(B^b_{1u})^2(A_u)^2(B_{1g})^2(B_{2u})^2(B^*_{3g})^1(B^*_{2g})^1(B^*_{1u}), \qquad \text{(V-48)}$$

resulting in two unpaired electrons for the iron complex- the observed value in the phenanthroline case. For a chromium (III) dimer with ten electrons, the electronic configuration is:

$$(B^b_{3g})^2(B^b_{2g})^2(B^b_{1u})^2(B_{1g})^2(A_u)^1(B_{2u})^1(B^*_{3g})(B^*_{2g})(B^*_{1u}), \qquad \text{(V-49)}$$

the complex is predicted to have two unpaired electrons. In each case the unpaired electrons are assumed to be in the non-bonding d_{xy} orbitals of appropriate symmetry. But such coupling is not observed and it must be concluded that strong π bonding is not an adequate explanation of the observed data.

If this statement is true, then the explanation must be found in the nature of the bridging groups and their effect through σ bonding. Evidence for the latter statement can be cited by considering the effective magnetic moment for the chromium (III) complexes Earnshaw and Lewis report, i.e. the phenanthroline, glycine, and phenylalanine, all strong field ligands, and this work in which a weak field ligand, water, is present: in all of these complexes chromium (III) can be seen to have three unpaired electrons per atom. Small J values are also observed. Since similar complexes for iron (III) - the phenanthroline and aquo complexes - show a considerable reduction in effective magnetic moment from a spin-free system and large J value, the effect must be associated with the bridging group common to both the Fe (III) and Cr (III) complexes. In Fe(III) complexes there are electrons in the σ bonding orbitals of proper symmetry to allow overlap with the hydroxide orbitals. This symmetry requirement is met whether sp^2 or pure p orbitals are postulated for oxygen. There is no <u>a priori</u> reasoning to allow π bonding through hydroxy bridges in the Fe(III) dimers and to disallow it for the Cr(III) dimers unless the bridging groups are different - e.g. oxygen bridges in Fe(III) dimers and hydroxide bridges in Cr(III) dimers. Metal-metal distances are of the same order of magnitude in both cases.

Similar arguments can be applied to the intermediate - a dimer formed by a single hydroxy bridge. From the values given in Table X, it can be

seen that the J value is somewhat larger and the effective magnetic moment of the intermediate reduced proportionately when compared to the blue dimer, implying that a somewhat larger coupling of spins has taken place. Although the Θ observed is much smaller than the analagous ammine complexes, the J value is found within the range of most chromium (III) dimeric species. The spectrum of the sample studied is essentially that of the dimer in high perchloric acid concentration, so the presence of monomer as an explanation for the small Θ value (Θ for the monomer is close to 0°) is ruled out.

The symmetry of the complex as a whole is C_s (Fig. 10b) because of the presence of the hydrogen on the bridging group while each individual chromium atom is in a crystal field of C_{4v} symmetry. In C_{4v} the s,p, and d orbitals of the metal atom transform as $3A_1 + B_1 + B_2 + 2E$, and the six σ bonds to the ligands as $3A_1 + B_1 + E$. Only the d_{xz}, d_{yx}, and d_{yz} orbitals are non-bonding, transforming as B_2 and E. In a crystal field of symmetry C_s, the non-bonding orbitals of both chromium atoms can then form the orbitals 2A' + 4A". The chromium atoms are even farther apart (4.06 Å) than in the doubly bridged dimer and again the orbitals would all be expected to be degenerate. However, interaction with π bonding orbital of the hydroxide ion which transforms as A" produces bonding and antibonding A" orbitals:

$$(A''^{b})(A''^{b})(A''^{b})(A''^{b})(A')(A')(A''^{*})(A''^{*})(A''^{*})(A''^{*}). \qquad \text{(V-50)}$$

Eight valence electrons, two from the hydroxide ligand and three from each of the chromium atoms occupy totally the bonding orbitals and the complex is then predicted to be diamagnetic.

Since the complex has not been found to be diamagnetic, the supposition of strong π bonding through the bridge is not supported. There

is a reduction in effective magnetic moment, however - somewhat larger than that observed in the doubly bridged dimer and the J value is correspondingly almost twice as large. This result may be related to the more favorable interaction of electrons through the bridge since an angle of 180° rather than 90° is presumed to exist in Cr-$\overset{H}{O}$-Cr group. No analagous complex of iron has been reported so the conclusions drawn cannot be tested as they were for the doubly bridged dimer. It must be supposed that a single hydroxy bridge produces a weaker field than two such bridges, and one would predict for analagous iron (III) complexes not so a large coupling of spins - perhaps close to the spin-free value for an individual iron (III) atom in an octahedral field.

(2) Trimeric Species

(a) Triangular Arrangement of Chromium Atoms - For the green trimeric species, two different assumptions were tested in an attempt to fit the data to a theoretical plot. Kambe's approach[34] using as a basis an equilateral triangle of chromium atoms was first tried. The basic Hamiltonian following from this assumption is:

$$= - 2 \{ J_{12}\underset{\sim}{S}_1 \cdot \underset{\sim}{S}_2 + J_{23}\underset{\sim}{S}_2 \cdot \underset{\sim}{S}_3 + J_{31}\underset{\sim}{S}_1 \cdot \underset{\sim}{S}_3 \} \qquad \text{(V-51)}$$

where J_{ij} refers to the exchange integral between the ith and jth ions, and $\underset{\sim}{S}_i$ is the spin vector on the ith ion. The J_{ij}'s and $\underset{\sim}{S}_i$'s are equal if the three ions composing the system are equivalent and arranged in the form of an equilateral triangle. A structure proposed for a trimeric chromium complex yielding such an arrangement is shown in Fig. 11a. Letting $\underset{\sim}{S}'$ equal $\underset{\sim}{S}_1 + \underset{\sim}{S}_2 + \underset{\sim}{S}_3$ and $\underset{\sim}{S}$ stand for $\underset{\sim}{S}_i$, the final expression for the Hamiltonian is:

$$= - J \{S'(S' + 1) - 3S (S + 1)\}. \qquad \text{(V-52)}$$

The expression for the variation of the atomic susceptibility with the temperature is given by:

$$\chi_A = \frac{g^2 N\beta^2}{3kT} \times 1/3 \times \left\{\frac{2 + 40\exp 3x + 105 \exp 8x + 168\exp 15x + 165\exp 24x}{2 + 80\exp 3x + 9 \exp 8x + 8\exp 15x + 5\exp 24x}\right\} + N(\alpha) \qquad \text{(V-53)}$$

where $x = J/kT$ and the other symbols have their usual meaning (cf. Eq. (6)). Figure 10 shows the plot of $1/X_A$ versus T for an equilateral triangle of chromium atoms with a g value of 1.94, the value determined for the green polynuclear species in the ESR measurements. The experimental points are indicated and it can be readily seen that the slope of the theoretical lines does not fit the experimental points.

(b) Linear Arrangement of Chromium Atoms - A second approach was tried assuming a linear arrangement of chromium atoms and bridging groups as shown in Fig. 11b. The essential Hamiltonian for this type of structure is given by

$$\mathcal{H} = -2\{J_{12}\underset{\sim}{S}_1 \cdot \underset{\sim}{S}_2 + J_{23}\underset{\sim}{S}_2 \cdot \underset{\sim}{S}_3\} \qquad \text{(V-54)}$$

where the J_{ij}'s have the same meaning as above. It is assumed that the exchange integral between the end and central chromium atoms will be the same for either end of the molecule and therefore that $J_{12} = J_{23} = J$, leading to the Hamiltonian:

$$\mathcal{H} = -2J\{\underset{\sim}{S}_1 \cdot \underset{\sim}{S}_2 + \underset{\sim}{S}_2 \cdot \underset{\sim}{S}_3\}. \qquad \text{(V-55)}$$

However, as before, the $\underset{\sim}{S}_i$'s$(i = 1,2,3)$ have the same magnitude and can be written as $\underset{\sim}{S}$. Then $\underset{\sim}{S}_i \cdot \underset{\sim}{S}_i = S(S + 1)$ and letting $\underset{\sim}{S}^* = \underset{\sim}{S}_1 + \underset{\sim}{S}_3$ and $\underset{\sim}{S}' = \underset{\sim}{S}_1 + \underset{\sim}{S}_2 + \underset{\sim}{S}_3$, the final expression for the Hamiltonian will be given by:

$$\mathcal{H} = -J\{S'(S'+1) - S(S+1) - S^*(S^*+1)\} \quad \text{(V-56)}$$

where $S^* = 2S, 2S-1, ..0$ and $S' = S^* + S, S^* + S - 1, ...|S^* - S|$, here, $S^* = 3,2,1,0$ and $S' = 9/2, 7/2, 5/2, 3/2, 1/2$. The variation of χ_A with temperature is then given by the following expression:

$$\chi_A = \frac{\frac{1}{4}xg^2N\beta^2}{3kT} \times \frac{165\exp 21x + 94\exp 18x + 35\exp 15x + 9\exp 12x + 35\exp 11x + 10\exp 10x}{5\exp 21x + 4\exp 18x + 3\exp 15x + 6\exp 12x + 3\exp 11x}$$

$$\frac{+\ \exp 3x + \exp 7x + 10\exp 6x + 35\exp 5x + 10}{+2\exp 10x + \exp 7x + 2\exp 6x + 3\exp 5x + \exp 3x} + N(\alpha)$$

Figure 10 shows the theoretical curve obtained from this expression, using the same g value of 1.94. The experimental points can be seen to lie on the curve corresponding to a J value of 21°. Table XI gives the experimental data used to calculate χ_A and Table XII the effective magnetic moment at 20°C, the g value, J, $N(\alpha)$ and θ observed for the green trimeric species.

Table XII. Reported Values of Susceptibility Parameters for Chromium (III) Trimer

Complex	μ_{eff} at 20°C (B.M.)	J	g	$N(\alpha)x10^6$	θ	Ref
$(aq)_4Cr(OH)_2\overset{aq}{\underset{aq}{Cr}}(OH)_2Cr(aq)_4$	3.31	-21	1.94	42	38°	This work

The only other trimeric chromium (III) species mentioned in the literature are those used in the measurements of Welo,[40] interpreted by Kambe in terms of an equilateral triangle of chromium atoms,[34] and those of Wucher and Gijsman.[41] In the latter instance the effective moment for the trimer $[Cr_3(CH_3COO)_6(OH)_2]Cl\cdot 8H_2O$ has been found to be 3.89 B.M. per chromium and yields a J value of -15°, assuming the three intersections

to be equal and using Kambe's definition of J. An attempt to consider one of the interactions as different from the other two indicated that the susceptibility is not particularly sensitive to variations in the J value associated with this added interaction. The Θ reported is based on measurements made very close to liquid helium temperatures, where a significant deviation (antiferromagnetic behavior) from measurements at higher temperatures is observed, and is of the order of 0.25°K. In the region of higher temperature, the Θ value is of the order of -90°K.

Kambe, using Welo's experimental data on a similar compound, $[Cr_3(CH_3COO)_6(OH)_2]Cl\cdot 8/3H_2O$ - Θ equal to -93°K - assumed an equilateral triangle of chromium atoms and found that a J value of 14° fitted his data. Welo's experimental data provided only a few points and Kambe's plot of μ_{eff} versus temperature is not a very sensitive criterion for agreement. However, Wucher and Gijsman's article indicates that a plot of $1/\chi_A$ (or $1/\chi_M$ as actually shown) can be closely fitted following the assumption of an equilateral triangle of chromium atoms for this particular complex. A g value of 2 is assumed in both treatments. Actually in these compounds the bridging groups are not identified nor is there any explanation offered for arrangement of ligands and metal atoms in the complex.

Considerations of symmetry in a linear complex of D_{2h} symmetry (Fig. 11b) show that the two end metal atoms are in a crystal field of C_{2v} symmetry while the central chromium is in a field of D_{4h} symmetry. In D_{4h} the s,p, and d orbitals have symmetry $2A_{1g} + A_{2u} + B_{1g} + B_{2g} + E_g + E_g + E_u$, while the same orbitals in C_{2v} have symmetry $4A_1 + A_2 + 2B_1 + 2B_2$. The six σ bonds to the chromium atoms are of symmetry $3A_1 + A_2 + B_1 + B_2$ and $2A_{1g} + A_{2u} + B_{1g} + E_u$ in C_{2v} and D_{4h}, respectively. The

d orbitals of chromium (III) which have not been used in σ bonding to the ligands are non-bonding orbitals: $A_1+B_1+B_2$ for the end atoms and $B_{2g} + E_g$ for the central atom. In D_{2h}, the nonbonding d orbitals transform as $B_{1g}+B_{2g}+B_{3g}$ and A_u, B_{1g}, B_{2g}, B_{1u}, B_{2u}, and B_{3g}, and these will probably all be degenerate because of the distance between chromium atoms. Since the π orbitals of the bridging groups transform as B_{2g}, B_{3g}, B_{1u} the orbital degeneracy should be split, yielding an energy level pattern:

$$(2B_{3g}^{b})(2B_{2g}^{b})(B_{1u}^{b})(A_u)(2B_{1g})(B_{2u})(2B_{3g}^{*})(2B_{2g}^{*})(B_{1u}^{*}), \qquad \text{(V-58)}$$

although the absolute order of level is unknown. There are seventeen valence electrons to be accomodated, three from each chromium and two from each hydroxy group, and the resulting electronic configuration is:

$$(2B_{3g}^{b})^4(2B_{3g}^{b})^4(B_{1u}^{b})^2(A_u)^2(2B_{1g})^2(B_{2u})^1(2B_{3g}^{*})(2B_{2g}^{*})(B_{1u}^{*}) \qquad \text{(V-59)}$$

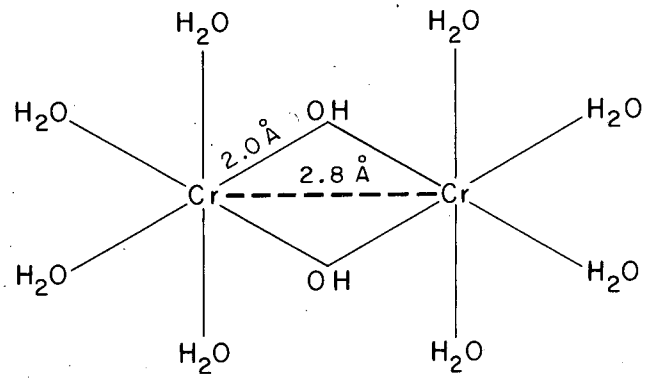
The complex is therefore predicted to have only one unpaired electron if strong π bonding is present. Such a large reduction in magnetic moment is not observed, the J value is comparatively small, and once again it can be stated that π bonding does not seem to play an important role in such hydroxy complexes.

(b) Conclusions - Perhaps the most significant conclusions that can be drawn from the discussion of these results is that the two dimeric species are indeed dimeric and represent chromium (III) atoms joined by hydroxy bridges. A single oxygen bridging group has been shown to produce a strong coupling in the basic rhodo complexes of chromium (III) and in such complexes as $Cl_5RuORuCl_5^{-4}$, and there is a marked change in the visible-UV spectra of the oxygen-bridged complexes. Some antiferromagnetic character ($J < 0$) can be attributed to the chromium polynuclear species reported here; but the coupling as measured by the J value indicates

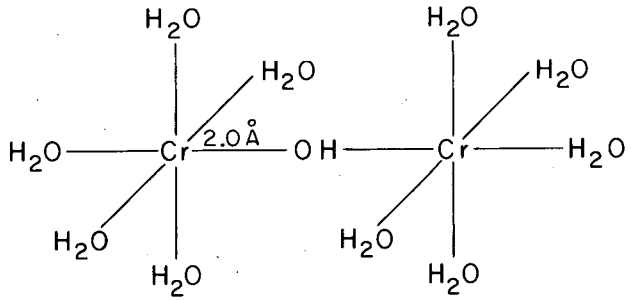
that the exchange interaction is of slight magnitude. Schaffer and Earnshaw and Lewis have offered as an explanation for the observed slight coupling in such chromium (III) complexes the deviation from 180° angle between Cr-O-Cr atoms when they are joined by a hydroxy rather than an oxygen bridge. However, Kobayashi, Haseda, Kanda, and Mori[42] postulate that the angle is almost 180° in the acid rhodo complexes they studied, even though there is a hydrogen on the bridging group.

The green polynuclear species has been shown to fit the susceptibility data as a linear trimer joined by hydroxy bridges. This is in a sense a more satisfying arrangement than an equilateral arrangement of chromium atoms since higher polymers of chromium (III) have been observed as bands adhering to an ion-exchange column under conditions where the green trimer is eluted. A linear arrangement is more satisfactory since the end of the chain is left open and additional chromium atoms can be linked to either end, thereby efficiently building up a chain polymer. This sort of behavior has been postulated for other metal ions in solution, e.g. Fe(III) and Al(III).

a.



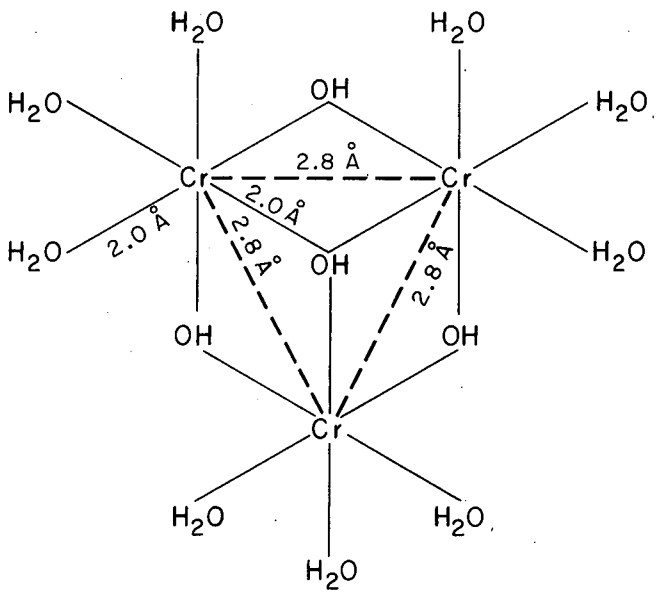
b.



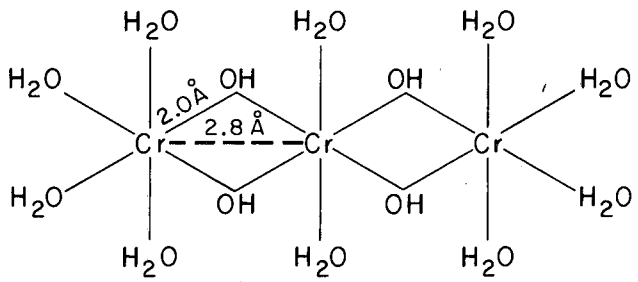
MU-34087

Fig. 10

a.

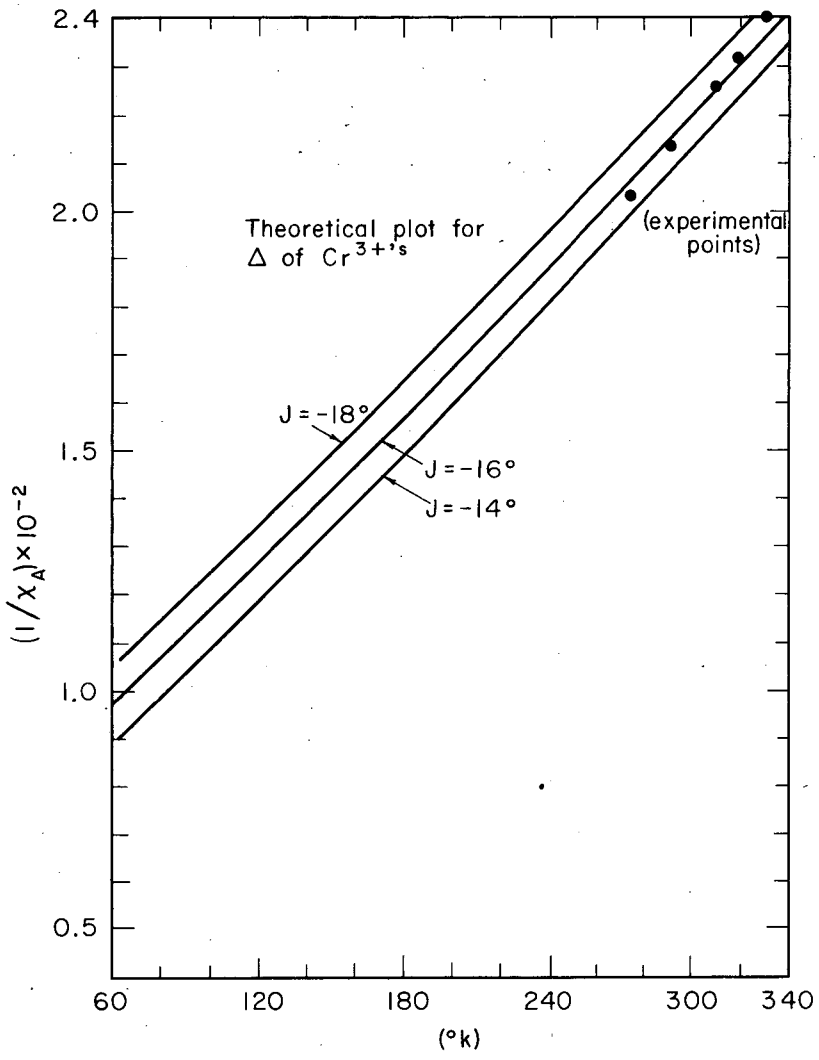


b.



MU-34088

Fig. 11



MU-34084

Fig. 12

3. Electron Spin Resonance Measurements of g Values

Figure 13 shows the electron spin resonance spectra obtained for the four species: monomeric chromium (III), the two dimers, $Cr_2(OH)_2^{4+}$ and $CrOHCr^{5+}$, and the trimer $Cr_3(OH)_4^{5+}$. The presence of some monomer in all samples of polynuclear species is not unexpected but does not exceed 1% in either the dimer or trimer samples. The intermediate was prepared from a concentrated dimeric sample, refrigerated for three days before use, and under the conditions of its preparation might be anticipated to contain a large quantity of monomer. The sharp-peaked spectrum of the monomer, nearly equivalent in height to the polymers themselves in the dimer and trimer spectra, is somewhat misleading if one supposed that the height of the signal is proportional to the concentration of the individual species. In derivative ESR signals such these the concentration is proportional to the square of the width times the height. Asymmetry of the polymer signal contributes additional complications to the resolution of the spectrum.

The g values computed from these studies are given in Table XIII.

Table XIII. g Values of Cr(III) Species in Perchloric Acid Solution at 20.0°C (ν = 9102.46 Mc)

Complex	g	H (in gauss)
monomer	1.980	157
dimer	1.976	~5x monomer
intermediate[a]	1.916	~4x monomer
trimer	1.942	479

[a] in concentrated perchloric acid

The g values might have been anticipated to lie close to the spin-only value of 2.002 since it can be shown for Cr(III)[43] in an octahedral field

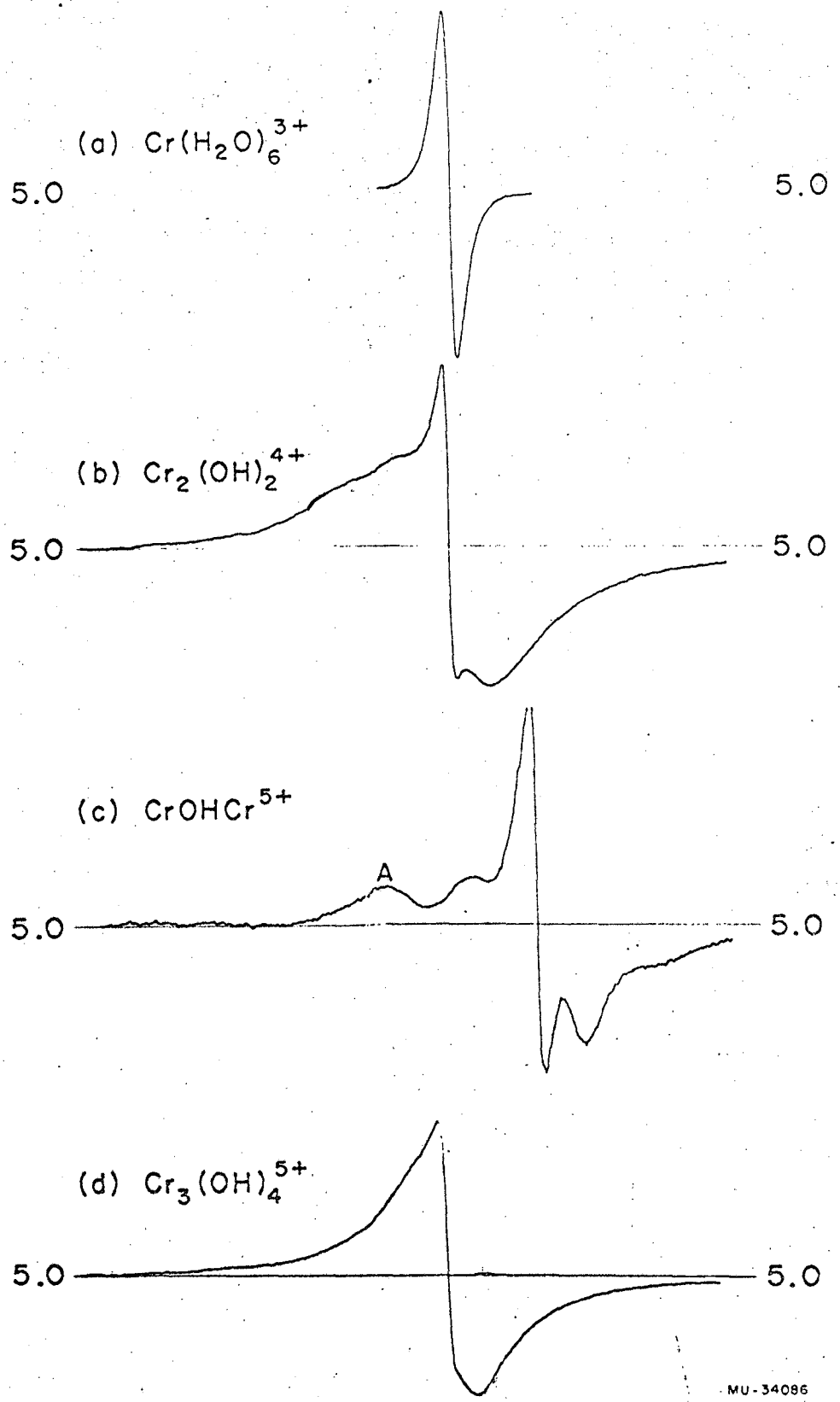


Fig. 13 ESR spectra of chromium (III) species
(A refers to an instrumental signal)

that

$$g = 2.002 - (8/3)(\lambda/\Delta) \qquad \text{(V-57)}$$

where λ is the spin-orbit coupling constant - positive for elements with less than half-filled shells - which is calculated from optical spectroscopy measurements and is reported as 273 cm^{-1} for Cr(III); and Δ, the ligand field splitting for octahedral complexes ($^4A_{2g}$ - $^4T_{2g}$ transition) which is of the order of 17,500 cm^{-1} for the chromium (III) complexes reported here. For F states g is expected to be isotropic and Cr(III) has a ground state of $^4F_{3/2}$. For all species studied in this work Δ shows only a slight variation and consequently no significant deviation from the calculated g of 1.960 would be anticipated. Clearly the approximations in the above formula are not adequate to explain the g values in detail.

It is difficult to draw any conclusions concerning the relaxation time since there are several factors contributing to the broadening effect which must be considered. It has been assumed that any anisotropy in the g values of the complexes has been cancelled by the rapid tumbling of the complexes, but such may indeed not be the case. Further studies would have to be carried out at other temperatures (practically, at higher temperatures) to observe change in the line width. Unfortunately this does not seem to be plausible for the blue dimeric species since preliminary studies show that it begins to convert to the monomer at more elevated temperatures and the line narrowing is obscured by the sharp resonance of the monomer. Intermolecular effects, comparable to concentration broadening, might also be a contributing factor.

An interesting sidelight resulting from these studies is the possibility of following the decomposition of the dimer to the monomer by changes in the line width. The very broad resonance of the dimer is

easily obscured by the sharp and very strong resonance signal of the monomer. Preliminary studies on the variation of line width with time point to the possibility of following the kinetics of decomposition by this means. Since a given temperature can be readily maintained and measured quite accurately, it should be an interesting and comparatively easy way to check the decomposition of the dimer at higher temperatures.

4. Attempts to Prepare Crystals

Fresh samples of the blue dimer were prepared by ion-exchange techniques and approximately 100 cc placed in a flash evaporator. The solution was allowed to evaporate under 200 microns of pressure to a final volume of 10 cc. Small portions of this material, ca. 4M in Cr(III), were added to concentrated perchloric acid and a fine blue, crystalline material was immediately formed. The green perchloric acid-Cr(III) supernatant was decanted off and the solid material resuspended in concentrated perchloric acid. The procedure was repeated until no trace of green appeared in the perchloric acid. The solid in contact with 11.6M perchloric acid was left at room temperature in a closed vessel and in a few hours' time the solution became colored a deep blue. The spectrum of the solution was imilar to that of the blue dimer although not identical.

The green supernatant formed crystals slowly on standing and the spectrum of these dissolved in both dilute and concentrated perchloric acid was that of the monomer. Powder patterns of both types of crystalline material were taken and the two materials found to be very different. Single crystal work on the purple cubic crystals from the green supernatant

established them as $Cr(H_2O)_6(ClO_4)_3$. A single crystal of the fine powder, hexagonal in form, was mounted in an x-ray capillary tube but turned brown under radiation. Further attempts to grow sufficiently large crystals of this material have been uniformly unsuccessful. The powder pattern is sharp but very complex.

During the course of preparation of a concentrated dimeric solution, it was found that the concentrated dimer crystallized in the flask as it was being evaporated under vacuum. The crystals formed were too small to furnish single crystals for x-ray work.

When 12 M lithium perchlorate was tried as a medium in which to form crystals of the dimer - a dependence on perchlorate ion concentration seems to be the essential factor in initial formation of the crystals - it was observed that only fine crystals of lithium perchlorate formed.

ACKNOWLEDGMENTS

I wish to express my very deep gratitude to Dean Robert E. Connick for his never-failing advice and help. It would indeed be difficult to find a better teacher and guide in the field of chemistry.

To my religious superiors whose decision it was that I begin this work and whose continued confidence in me has contributed to its completion; to the Sisters of the Presentation who have supported me with their friendship and kindness during the years of study and research; to my fellow graduate students for many helpful and stimulating discussion; and to Mrs. Patricia Cookson for her monumental secretarial help in preparing this thesis, special thanks are due.

I also wish to thank Professor Rollie Myers and Brock Spencer for obtaining the ESR spectra.

Financial support was received from the United States Atomic Energy Commission through the Lawrence Radiation Laboratory.

FIGURE CAPTIONS

Fig. 1 Absorption spectra of Cr(III) species.

Fig. 2 Energy level diagrams for (a) dimeric species and (b) a linear trimer.

Fig. 3 A plot of 1/T versus log K for K_{22} and K_{34}.

Fig. 4 Change in absorbance at 2700 Å of the blue species in 7.6 M $HClO_4$ with time (25.0°C).

Fig. 5 A plot of A-0.932 of the first step in the decomposition of the blue species in 7.6 M $HClO_4$ (25.0°C).

Fig. 6 Change in absorbance at 2700 Å for the dilution of acidified solution of blue dimer.

Fig. 7 A plot of 0.822 - A_t for formation of blue dimer from intermediate.

Fig. 8 A plot of $k_{observed}$ versus perchloric acid or a function of temperature and ionic media.

Fig. 9 A plot of $1/\chi_A$ versus T.

Fig. 10 Proposed structures for dimeric species: (a) the blue species (D_{2h}) and (b) the intermediate (C_s).

Fig. 11 Proposed structures for a trimeric species: (a) an equilateral triangle of chromium atoms and (b) a linear arrangement of chromium atoms.

Fig. 12 A theoretical plot of $1/\chi_A$ vs T for an equilateral triangle of chromium atoms.

Fig. 13 ESR spectra of chromium (III) species.

REFERENCES

1. L. G. Sillen, Quart Rev. 14, 147 (1959).
2. R. W. Holmberg, K. A. Kraus, and J. S. Johnson, J. Am. Chem. Soc. 78, 5506 (1956).
3. R. S. Tobias and S. Y. Tyree, Jr., J. Am. Chem. Soc. 82, 3244 (1960).
4. L. N. Mulay and P. W. Selwood, J. Am. Chem. Soc. 76, 6207 (1954).
5. E. L. King, S. M. J. M. Woods, and H. S. Gates, J. Am. Chem. Soc. 80, 5015 (1958). (See also refs. 16 and 17).
6. B. O. A. Hedstrom, Arkiv Kemi 5, 457 (1953).
7. T. H. Siddell and W. C. Vosburgh, J. Am. Chem. Soc. 73, 4270 (1951).
8. D. M. Grant and R. E. Hamm, J. Am. Chem. Soc. 80, 4166 (1958).
9. T. J. Swift and R. E. Connick, J. Chem. Phys. 37, 307 (1962).
10. H. Taube, Chem. Rev. 50, 69 (1952).
11. N. Bjerrum, Studiere over Basiske Kromiforbindelsen, Dissertation, Copenhagen, 1908.
12. E. Stiasny and D. Balanyi, Collegium, 1927, 86.
13. R. Schaal and J. Faucherre, Bull. Soc. Chim. France, 14, 927 (1947).
14. P. Souchay, Bull. Soc. Chim. France 15, 143 (1948).
15. H. T. Hall and H. Eyring, J. Am. Chem. Soc. 72, 782 (1950).
16. J. A. Laswick and R. A. Plane, J. Am. Chem. Soc. 81, 3564 (1959).
17. J. E. Finholt, Lawrence Radiation Laboratory Report, UCRL-8879, (1960).
18. M. Ardon and A. Linenberg, J. Phys. Chem. 65, 1443 (1961).
19. M. Ardon and R. A. Plane, J. Am. Chem. Soc. 81, 3197 (1959).
20. R. W. Kolaczkowski and R. A. Plane, Inorg. Chem 3, 322 (1964).

21. R. K. McMullan and J. D. Corbett, J. Chem. Educ. 33, 313 (1956).

22. C. Postmus and E. L. King, J. Phys. Chem. 59, 1208 (1955).

23. G. Mattock, pH Measurement and Titration, McMillan and Co., (1961).

24. J. Y. Tong and E. L. King, J. Am. Chem. Soc. 75, 6180 (1953).
H. A. C. McKay in Proceedings of Symposium on Coordination Chemistry 1953, Copenhagen: Danish Chemical Society, 1954.

25. G. Parissakis and G. Schwarzenbach, Helv. Chim. Acta, 41, 2042 (1958); 41, 2425 (1958).

26. A. Earnshaw and J. Lewis, J. Chem. Soc. 1961, 396.

27. R. A. Milburn, J. Am. Chem. Soc. 79, 537 (1957).

28. R. E. Hester and R. A. Plane, Inorg. Chem. 3, 769 (1964).

29. W. K. Wilmarth, H. Graff, and S. T. Gustin, J. Am. Chem. Soc. 78, 2683 (1956).

30. R. E. Powell, J. Phys. Chem. 58, 528 (1954).

31. T. B. Joyner and W. K. Wilmarth, J. Am. Chem. Soc. 83, 516 (1961).

32. H. Stone, J. Am. Chem. Soc. 58, 2591 (1936); H. Stone reported in the Abstracts of the 141st meeting of the American Chemical Society.

33. B. N. Figgis and J. Lewis in Modern Coordination Chemistry, J. Lewis and R. Wilkins (eds.), Interscience Publishers, New York (1960).

34. K. Kambe, J. Phys. Soc. Japan 5, 48 (1950).

35. L. M. Mulay and M. C. Naylor in Advances in the Chemistry of the Coordination Compounds, S. Kirchener (ed.), MacMillan, New York, 1961.

36. E. N. Sloth and C. S. Garner, J. Phys. Chem. 56, 2064 (1956).

37. C. E. Schaffer and C. K. Jorgensen, J. Inorg. Nucl. Chem. 8, 143 (1958).

38. L. N. Mulay and P. W. Selwood, J. Am. Chem. Soc. 77, 2693 (1955).

39. N. Elliott, J. Chem. Phys. 35, 1273 (1961).

40. L. A. Welo, Phil Mag. 7th Ser. 6, 481 (1928).

41. J. Wucher and H. M. Gijsman, Physica 20, 36 (1954).

42. H. Kobayashi, T. Haseda, E. Kanda, and M. Mori, J. Phys. Soc. Japan 15, 1646 (1960).

43. C. K. Jorgensen, Absorption Spectra and Chemical Bonding in Complexes, Addison-Wesley, Reading, Massachusetts, 1962.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

LRL